Vol. XX

# THE PHYSICAL REVIEW

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THE

# PHYSICAL REVIEW.

## ON THE NATURE OF THE NEGATIVE AND POSITIVE IONS IN AIR, OXYGEN AND NITROGEN.

By Henry A. Erikson.

Synopsis.

*Positive and Negative Ions in Air, Oxygen and Nitrogen.*—(1) *Mobilities just after formation* were measured by using a modified form of Zeleny's blast method. Ions produced in air by polonium rays were drawn immediately by a current of 470 cm./sec. into one side of a cross field of 130 volts/cm. and the distance they were carried along before they were dragged to the other side by the field was determined. When the average age of the ions was about 0.03 sec. the mobility was found to be the same for both positive and negative ions and equal to that for normal negative ions, about 1.89 cm./sec./volt/cm. As the age was increased to 0.5 sec., however, the positive mobility decreased to its normal value, about 1/1.40 times the negative mobility. The same results were obtained with dry commercial oxygen and nitrogen, except that the aging of the positive ion was more rapid in oxygen. (2) *Nature of the ions.* In explanation of the above results it is suggested that the negative ion and the initial positive ion are each one molecule in size and that the permanent positive ion is two molecules in size. This suggestion agrees with the view that when ionization occurs an electron is ejected from a molecule, leaving a positively charged molecule, an initial positive ion, which does not immediately acquire the second molecule needed to form a permanent positive ion. The electron attaches itself to a molecule and forms a permanent negative ion. It is also shown that the observed ratio of the mobilities for ions with one and two molecules respectively agrees with that computed according to the small ion theory of Wellisch.

THE nature of the positive and negative ions produced in air by an ionizing agent is a question of considerable interest. It has not been easy to obtain conclusive evidence.

In 1900 Zeleny[1] succeeded in determining the absolute values of the mobilities of the ions in question. The values found were, for the negative ion 1.87 cm./sec./volt/cm., and for the positive ion 1.36, giving the ratio of the negative mobility to the positive of 1.375.

Each of the above ions forms a stable unit. The ratio 1.375 shows that these units are not alike. To what this difference is due is a question of interest.

[1] Phil. Trans. A, Vol. 195, p. 193.

About two years ago[1] it occurred to the writer to try a modified form of Zeleny's blast method.

The experimental arrangement was as indicated in Fig. 1. $A$ and $B$

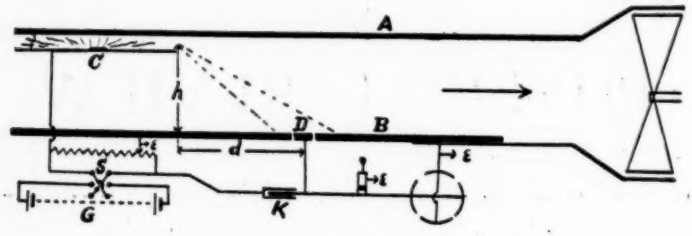



Fig. 1.

were two parallel plates 5 cm. wide, 40 cm. long and 4.5 cm. apart. $C$ was a plate about 12 cm. long placed about 0.6 cm. below $A$. $A$ and $C$ were connected. $D$ was a narrow insulated strip placed in the plane of $B$ and connected to a quadrant electrometer. The plate $B$ and strip $D$ were movable so that the down stream distance of $D$ could be altered. The sides of the apparatus were of glass.

Air from the room was drawn through this rectangular tube by means of a fan driven by a synchronous motor. Plate $B$ was kept at zero potential while $A$ was raised to the potential of the battery $G$. In order to compensate for any change in the voltage of the battery $G$ during readings the air condenser $K$ was introduced.

A polonium plate was placed at $C$, the rays from which ionized the air between plates $C$ and $A$. As $A$ and $C$ were connected there was no field causing the ions to move to the plates. The ions were carried by the air to the mouth of this chamber where they entered the field between $A$ and $B$. If $A$ were positive the positive ions were driven to $B$, and negative to $A$.

By changing the down stream distance of the strip $D$ the current at the different points on $B$ could be measured. For each position of the strip $D$ both the positive and negative currents were measured by reversing $S$ leaving the conditions otherwise unchanged.

The velocity of the air was obtained by means of an anemometer. The times for a given deflection of the electrometer for the positive and negative currents at different positions of $D$ were obtained. Upon plotting the reciprocals of these times against the down stream distances of $D$ as abscissæ, the curves shown in Fig. 2 were obtained:

To the writer's surprise these two curves were found nearly to coincide, indicating equal mobilities of the positive and negative ions. The average age of the ions in this case was of the order of 0.03 second.

[1] PHYS. REV., (2) XVII., p. 400; (2) XVIII., p. 100.

The spreading of the curves is due primarily to the slant of the plate $B$ with reference to the direction of the ionic stream. By projecting on a plane at right angles to the ionic stream the spreading is of the order

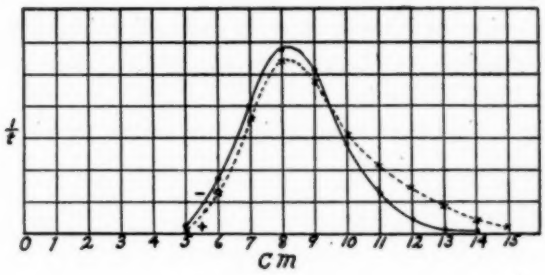



Fig. 2.

of 3 cm. instead of 8 cm. The amount of spreading due to the self repulsion of the ions is, on each side, of the order of 0.5 cm., about the thickness of the current sheet. Deducting this will reduce the spreading to about 1.5 cm. which is undoubtedly due mainly to air turbulence. Excessive air turbulence was however not present. This was determined by means of smoke streams. The factors given above are of an order such as to preclude the necessity of attributing the spreading to non-homogeneous ions.

The absolute value of the mobility may be determined as follows: Let $h$ be the average distance the ion travels at right angles to the stream of air and $d$ the distance it travels down stream in the same time $t$. Then

$$h = k\frac{V}{H}t,$$

but

$$t = \frac{d}{v};$$

$$\therefore \quad k = \frac{hHv}{Vd},$$

where $H$ = distance between the plates $A$, $B$,
$V$ = difference of potential between plates $A$, $B$,
$v$ = velocity of air,
$k$ = mobility of ion.

The mobility $k$ therefore varies inversely as the down stream distance $d$. The ratio of two mobilities therefore is

$$r = \frac{k_1}{k_2} = \frac{d_2}{d_1}.$$

If two ions have the same mobility their down stream distances $d$ are the same.

As the curves for the positive ion and the negative ion came superimposed, the conclusion must be that both ions had the same velocity.

The next question of interest was to determine if the mobility represented by the maxima of the curves was the normal mobility for the negative or for the positive ion.

The following values for the quantities necessary for the determination of the mobility were obtained:

$V = 535$ volts,
$d = 8.2$ cm. (using maximum of curve),
$h = 4.2$ (using same average value for $H$),
$v = 470$ cm./sec.

The above values gives for the mobility

$$k = 1.89 \text{ volt/cm.}$$

As this is of the order of the normal value for the mobility of the negative ion, the necessary conclusion is that the positive ion involved had the same mobility as the normal negative ion.

In order to determine if the age of the positive ion had any effect an extension was added as shown in Fig. 3. The polonium plate was placed

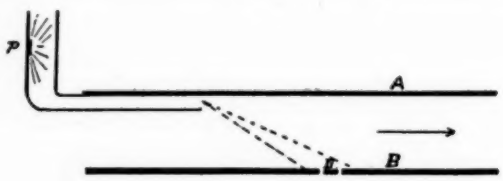



Fig. 3.

at $P$ so that the ions were of the order of 0.5 second old when they entered the field at $B$. The air velocity remained the same as before.

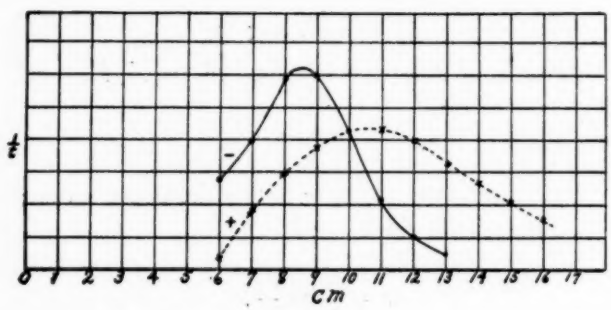



Fig. 4.

The curves obtained for the positive and negative ions are shown in Fig. 4. As the maximum for the negative ion remained unchanged it became evident that the poistive ion had undergone a change during the first fraction of a second of its life as its maximum had shifted down stream indicating a slower ion.

The same change was obtained when the ions were aged by reducing the velocity of the air, the polonium plate being at *C*, Fig. 1. The curves *A* and *B* in Fig. 5 were obtained in this manner. The ratio of the initial

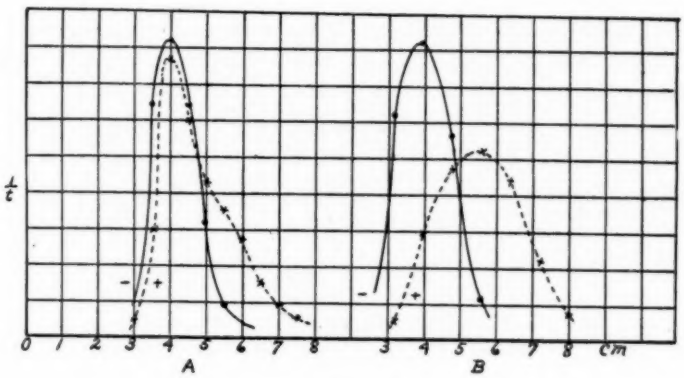



Fig. 5.

mobility to the final mobility is

$$\frac{k_1}{k_2} = \frac{5.5}{3.9} = 1.40$$

which is about the normal ratio for air.

The significance of the above must be that the negative and positive ions are initially alike in magnitude and that the positive ion soon increases to a larger stable unit.

In order to determine if this effect is peculiar to air the apparatus was enclosed so that oxygen and nitrogen could be investigated separately.

The gases were obtained from commercial supply tanks and were dried by passing through $CaCl_2$. The gases were not of a high degree of purity. The ions were aged by reducing the gas velocity.

The curves obtained are given in Fig. 6.

The results obtained show that in oxygen and nitrogen, of the purity involved, the negative ion does not change. The positive ion, however, does in each case undergo a change. It is also observed that the change in the mobility of the positive ion in oxygen is somewhat more rapid than in nitrogen.

*Statement of Hypothesis.*—In explanation of the above it seems most

reasonable to take the molecule as the unit in terms of which the change takes place. On this basis the simplest hypothesis becomes as follows:

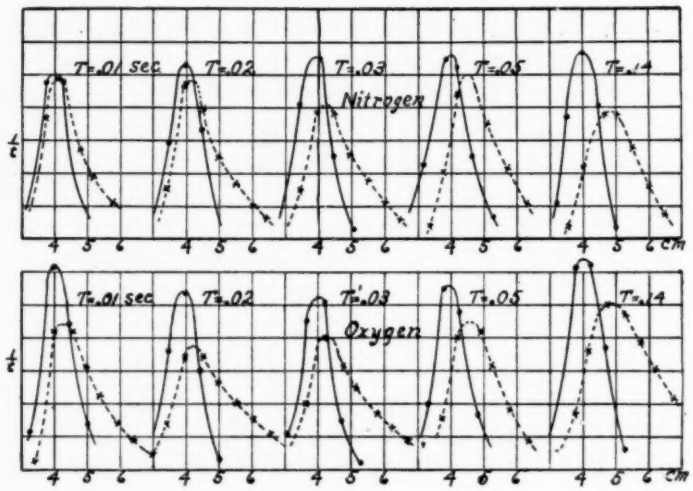



Fig. 6.

In the process of ionization of air one of the atoms of the nitrogen or oxygen molecules is caused to eject an electron, the molecule otherwise remaining intact. The electron remains free on the average a very small fraction of a second especially in the presence of oxygen. It soon attaches itself to a neutral molecule and this combination forms the negative ion. The positive remainder of the molecule which ejected the electron constitutes the initial positive ion. As the two above ions have the same mass and charge their mobilities are equal. The initial positive ion, however, soon attaches itself to a neutral molecule forming the permanent positive ion. Since its mass is twice as great as the initial positive ion or the negative ion, it has a smaller mobility.

*Evidence in Support of Hypothesis.*—It is of interest to consider the above hypothesis in connection with the small ion theory proposed and developed by Wellisch.[1] In this theory it was shown that the collision distance $\sigma$ existing between two uncharged molecules, changes to

$$\sigma[1 + 2R/mv^2]^{1/2}$$

when one of the molecules is charged. $R$ denotes the potential due to the polarization of the neutral molecule by the charge on the ion, and its value is shown to be

$$R = \frac{2(K-1)e^2}{\pi n(S+S^1)^4},$$

[1] Phil. Trans. A, Vol. 209, p. 249.

where $S$ and $S^1$ are the diameters of the force spheres of the molecule and ion respectively, $K$ is the specific inductive capacity, and $e$ the charge.

The collision distance thus becomes

$$\sigma\left[1+\frac{4(K-1)e^2}{\pi n m v^2 (S+S)^4}\right]^{1/2}.$$

The expression for the reciprocal of the mean free path is

$$L^{-1} = \pi n\left[1+\frac{M}{m}\right]^{1/2}\sigma^2.$$

This when the new expression for $\sigma$ is introduced becomes

$$L^{-1} = \pi n\left(1+\frac{M}{n}\right)^{1/2}\sigma^2\left[1+\frac{4(K-1)e^2}{\pi n m v^2 (S+S^1)^4}\right].$$

Substituting this in Langevin's expression for the mobility, namely

$$k = \frac{eL}{MV}$$

gives on the basis of equipartition of energy

$$k = \frac{A\eta}{\rho p}4\sqrt{2}\left(\frac{m}{M}\right)^{1/2}\left(1+\frac{M}{m}\right)^{-1/2}\left(1+\frac{S^1}{S}\right)^{-2}\left[1+\frac{4(K-1)e^2}{\pi n m v^2 (S+S^1)^4}\right]^{-1},$$

where $M$ = the mass of the ion,
$m$ = the mass of the molecule,
$S^1$ = diameter of force sphere of ion,
$S$ = diameter of force sphere of molecule.

The ratio of two mobilities becomes:

$$\frac{k_1}{k_2} = \frac{\left(\frac{m}{M_1}\right)^{1/2}\left(1+\frac{M_1}{m}\right)^{-1/2}\left(1+\frac{S_1}{S}\right)^{-2}\left[1+\frac{4(K-1)e^2}{\pi n m v^2 (S+S_1)^4}\right]^{-1}}{\left(\frac{m}{M_2}\right)^{1/2}\left(1+\frac{M_2}{m}\right)^{-1/2}\left(1+\frac{S_2}{S}\right)^{-2}\left[1+\frac{4(K-1)e^2}{\pi n m v^2 (S+S_2)^4}\right]^{-1}}.$$

Using Wellisch's values of

$$3.70 \text{ for } \frac{(K-1)e^2}{4\pi n m v^2 S^4}$$

and placing $S' = aS$ and $M = bm$, the above ratio becomes

$$\frac{k_1}{k_2} = \frac{\sqrt{b_2}\sqrt{1+b_2}\,(1+a_2)^2\left[1+\frac{59.2}{(1+a)^4}\right]}{\sqrt{b_1}\sqrt{1+b_1}\,(1+a_1)^2\left[1+\frac{59.2}{(1+a)^4}\right]}.$$

Let $k_1$ = mobility of ion of mass $m$, *i.e.*, $M_1 = m$, $S_1 = S$; then $a_1 = 1$, $b_1 = 1$ and

$$\frac{k_1}{k_2} = \frac{\sqrt{b_2}\,\sqrt{1 + b_2}(1 + a_2)^2\left[1 + \frac{59.2}{(1 + a_2)^4}\right]}{26.6}.$$

The above expression may be written

$$\frac{k_1}{k_2} = \frac{\sqrt{b_2}\,\sqrt{1 + b_2}\,J}{26.6},$$

where $J$ is a function of $a_2$. The function $J$ is a minimum for

$$a_2 = 1.77.$$

Using this value of $a_2$ in $J$, for the ion of mass $M_2 = 2m$, *i.e.*, $b = 2$, gives for the ratio

$$\frac{k_1}{k_2} = 1.418.$$

It is thus seen that the initial ion of $M_2 = m$ and final ion of $M = 2m$ of the hypothesis gives a mobility ratio of 1.418 when the diameter of the force sphere of the final ion is 1.77 times that of the molecule $m$. This is in satisfactory agreement with the observed ratio 1.40.

It is necessary to determine if other values of $b$ and $a$ will give the observed ratio 1.40.

Since $J$ is a minimum for $a = 1.77$ it is evident that values of $M_2$ greater than $2m$ will give ratios which for all values of $a_2$ will be too large. For values of the mass of the ion less than $2m$, only two cases are possible namely, $M_2 = m$ and $M_2 = 3/2m$ (three atoms). For each of these there are two values of $a_2$ either of which will give the observed mobility ratio as may be found by substituting 1.40 for the ratio and solving for $a_2$. These are

$$a_2 = 0.58 \text{ and } 3.87 \text{ for } M_2 = m$$

and

$$a_2 = 0.96 \text{ and } 2.92 \text{ for } M_2 = 3/2m.$$

As the change in size is of the nature of an addition to the solid kernel, the charge remaining the same, the above values are quite untenable. The observed ratio is therefore obtained only in the case of an ion two molecules in size.

Since $\sqrt{2m/m} = \sqrt{2} = 1.414$, is in fair agreement with the observed ratio of the mobilities, the above suggests that in any one gas the mobility is approximately proportional to the inverse square root of the mass of the ion.

The velocity in the direction of the field $X$, obtained by an ion in the time $t$, is

$$v = \frac{Xe}{M}t,$$

where $t$ is the mean free time between collisions. The average velocity of drift will therefore be

$$\bar{v} = \frac{Xe}{2M}t$$

and the mobility, which is the coefficient of $X$, is

$$k = \frac{e}{2M}t.$$

The value of $t$ is determined by the velocity of temperature agitation and the velocity, which is superimposed, due to the field. As the former is large compared to the latter, $t$ may be regarded as entirely determined by the velocity of temperature agitation $V$. We may consequently write

$$t = \frac{\lambda}{V},$$

where $\lambda$ is the mean free path of the ion.

The mobility then is

$$k = \frac{e\lambda}{2MV}.$$

Substituting, on the basis of equipartition of energy, the value of $V$ obtained from the relation

$$1/2MV^2 = 3/2RT$$

gives the mobility

$$k = \frac{e\lambda}{2\sqrt{M}\sqrt{3RT}}.$$

The ratio for two sets of ions then becomes

$$\frac{k_1}{k_2} = \frac{\sqrt{M_2}\lambda_1}{\sqrt{M_1}\lambda_2}.$$

The statement that the ratio of the mobilities of two ions in any one gas is proportional to the inverse ratio of the square root of their masses, therefore requires that their mean free paths be the same. This would be the case if the mean free path is determined primarily by the charge.

The indication of all the above is that the final positive ion has a mass which is twice the mass of the initial positive ion.

The question then becomes: Is one justified in assuming that the initial positive ion is one molecule in size? It is evident that this question must be answered through a knowledge of the ionization process.

The strongest evidence at the present time is the existence of free electrons at the instant of ionization. The results obtained by Franck, Haines, Wellisch, Loeb and others are conclusive on this point. On the strength of this we would conclude that the ionization process consists in the ejection of an electron. The next obvious step is to assume that the electron attaches itself to a neutral molecule rather than an atom. The chance of the first must be very much greater than the second. If this takes place then the negative ion is one molecule in size. If it is larger than one molecule the early transition stages should be detectible experimentally. Different transition stages have not been observed in these experiments.

If the negative ion is one molecule in size then the initial positive ion must be one molecule in size, since their mobilities are the same.

As shown above the indications are that the final positive ion is two molecules in size. If it is larger than this the transition stages should be detectible experimentally. This in connection with the ion in question is not observed in this investigation.

It is of interest to note that on the basis of the above, the mobilities 1.32, 1.53, 1.87, 2.64 may be predicted corresponding respectively to the ions of masses, two molecules, three atoms, one molecule, one atom.

There has just come to my hands a paper by Nolan and Harris[1] in which results are given which are interpreted as indicating the presence of several mobilities. Among these for the positive as determined by a blast method are

$$(2.5),\ 2.04,\ 1.79\ 1.52\ 1.37.$$

Evidence of 2.5 was only obtained by an A.C. method. Of these five values four are predicted by the above.

I am glad to take this opportunity of expressing my indebtedness to Professor W. F. G. Swann and to Professor John T. Tate for their helpful suggestions and kind interest.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
March 9, 1922.

[1] Proc. Roy. Irish Acad., XXXVI., A, 2, p. 31.

# PHENOMENA IN GASES EXCITED BY RADIO FREQUENCY CURRENTS.

BY E. O. HULBURT.

SYNOPSIS.

*Undamped Radio Frequency Vacuum Discharges through Hydrogen, Oxygen and Air.*—(1) *The spectra*, 5000–3500 Å., were found to be the same for frequencies of $3 \times 10^5$ to $4 \times 10^6$ as for 60 cycles, with currents of the same strength. (2) *The minimum discharge potentials* for electrode distances from 5 to 30 mm. and pressures of from 1 to 5 mm. of mercury were also found to be independent of the frequency and the same as for direct currents. A theoretical discussion of this result leads to the conclusion that the discharge is initiated by collisions of electrons, rather than of gaseous ions, with gas molecules. (3) *Persistence* of each discharge was studied with the aid of a mirror rotating 200 times per second. Damped discharges with a frequency of $10^6$ cycles or less showed separate flashes but those with higher frequencies were blended together. This difference may perhaps be due to the limitations of the apparatus used. With damped oscillations the color of the discharge changed with the voltage as would be expected.

## INTRODUCTORY.

LITTLE is known of the behavior of gases stimulated into luminosity by alternating electric currents of radio frequency and the present investigation was undertaken for the purpose of obtaining information on this subject. By radio frequency we mean the range of frequencies usually employed in the radio art, *i.e.*, the range between $10^5$ and $10^7$ alternations per second. The description of the work is taken up in three parts as follows, the radio frequency spectra, the potentials necessary to set up luminosity, and the radio frequency flashes of light.

## THE RADIO FREQUENCY SPECTRA.

Numerous experiments on electrically excited gases have been performed concerning the relations between the type of electrical excitation and the spectrum of the luminous gas and in some cases[1] potentials alternating at radio frequencies have been used. Recently Dunoyer[2] has discovered new spectra from certain metallic vapors by the use of damped radio frequency currents. None of these experiments, however, tell definitely the effect, if any, on the spectrum of the gas occasioned by the frequency of the alternating current. The advent of the oscillating electron-tube methods of generating radio frequency currents has ren-

[1] Wiedemann and Ebert, Wied. Ann., 50, 221, 1893; Himstedt, Wied. Ann., 52, 473, 1894.

[2] Comptes Rendus, 173, 350, 1921; 173, 472, 1921.

dered possible a direct answer to this question and the present work has been undertaken with this in view. It may be stated in advance that for the cases here investigated the spectrum of the gas remained unchanged when the frequency was increased from sixty to a million or more cycles per second, other factors being kept constant.

An electron-tube oscillating circuit was arranged for the production of currents of frequencies from $0.43 \times 10^7$ to $10^5$ cycles per second, *i.e.*, wave-lengths from 70 to 3,000 meters. The tube was a fifty watt power tube with 1,000 volts on the plate and a filament current of 6.5 amperes. By means of this generating circuit radio frequency current could be induced in coil *b*, Fig. 1, which was in series with a variable air condenser *c* and a hot wire ammeter *a*. By means of a switch *s* the end-on discharge tube *d*, which was in series with the thermogalvanometer *t*, could be connected either across *c* or to the high potential terminals of a ½ kw., 25,000 volt transformer *p* actuated by 60-cycle current. The discharge

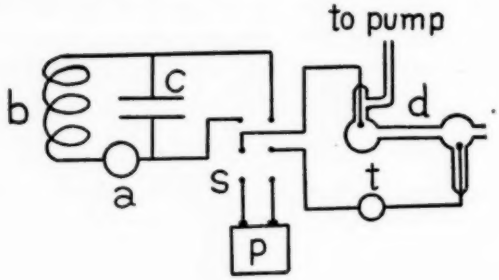



Fig. 1.

tube was of glass with aluminum electrodes arranged out of line with the capillary. The capillary was 10 cm. long and with an internal diameter of 5 mm. Hydrogen, oxygen, and air, purified by sodium hydroxide solution, sulphuric acid and phosporous pentoxide, at a pressure of 3 mm. or less were used in the tube. The generating circuit and the circuit *bc* were tuned to the desired frequency. With 4 amperes through *a* and with *c* adjusted to, say, 500 $\mu\mu F$, the discharge tube glowed brilliantly. The increase in the current through the tube when luminosity occurred was about one half of a milliampere. When the 60-cycle transformer was used the current through *t* was adjusted to be one half of a milliampere.

The spectra were photographed throughout the region from 5000 A to 3500 A in the first order of a concave grating of two meters radius of curvature ruled 14435 lines to the inch. The spectra of hydrogen, oxygen and air excited by currents of frequencies 60, $3 \times 10^5$, $10^6$ and $0.43 \times 10^7$ were recorded, and in all cases the spectrum was found to be

unmodified by the change in frequency. With hydrogen about three hundred lines of the secondary spectrum and a faint continuous background appeared on the plates. The Balmer lines were faint. Oxygen exhibited the fine-lined band spectrum. Air showed the oxygen and nitrogen lines.

## The Potential Necessary to set up Luminosity.

Measurements of the potentials just sufficient to set up luminosity in a gas for radio frequency and direct currents yielded information concerning the cause of the luminosity. For this purpose a bulb was equipped with disc electrodes 1.5 cm. in diameter whose distance apart could be varied. The potential difference of the electrodes was measured by an electrostatic voltmeter. The maximum reading of the instrument was 1,000 volts and above 200 volts the indications were accurate within 10 volts. To make a measurement the potential difference of the electrodes was increased very slowly and the voltage observed when the bulb suddenly burst into luminosity. Table I. shows a series of readings for hydrogen when the electrodes were 14 mm. apart. In the table the numbers for the alternating voltages were the maximum values of the voltages, and were obtained by multiplying the electrometer readings by $\sqrt{2}$. The conclusion from Table I. and from similar

Table 1.

| Pressure in Mm. of Hg. | Frequency. | | | |
|---|---|---|---|---|
| | 0 | 60 | $0.86 \times 10^6$ | $5.3 \times 10^6$ |
| 3.4 | 640 volts | 635 | 652 | 642 |
| 2.0 | 430 | 436 | 436 | 424 |
| 0.9 | 410 | 424 | 404 | 409 |

tables for hydrogen and oxygen, for electrode distances from 5 to 30 mm. and for pressures from 1 to 5 mm. of mercury, was that for a specified electrode distance and gas pressure the voltage just sufficient to produce luminosity did not change when the frequency was varied over a wide range.

We turn to a consideration of the electron theory in this connection. It is known that luminosity is set up when collision occurs between a molecule of the gas and an electron or ion which has acquired a certain critical velocity. A molecule or atom may acquire sufficient energy to become luminous not only by a single violent encounter but also by the accumulation of energy from a succession of milder encounters. It is

reasonable to suppose that the luminosity is *begun* by a single violent encounter, for this process is conceivably much quicker than the other. We proceed to find an expression for the critical velocity of the ion partaking in the violent encounter in the case of a steady electric field and of an alternating electric field.

We assume a Lorentz contractile electron of charge $e$ and mass $m$ for small velocities. The electron moves from rest under the influence of a homogeneous steady electric field $E$ which is in the direction of the $X$ axis. The effects on the motion due to radiation from the accelerated electron are neglected. If c.g.s. electromagnetic units are used the equation of motion of the electron is in Newtonian notation

$$\ddot{x} = E\frac{e}{m}\left(1 - \frac{\dot{x}^2}{c_2}\right)^{3/2}, \tag{1}$$

where $x$ is the positional coördinate of the electron, and $c$ is the velocity of light *in vacuo*. With initial conditions $t = x = \dot{x} = 0$, the solution of (1) is found to be

$$x = \frac{ct}{\sqrt{\frac{c^2m^2}{E^2e^2} + t^2}} \tag{2}$$

and

$$x = c\sqrt{\frac{c^2m^2}{E^2e^2} + t^2} - \frac{c^2m}{Ee}. \tag{3}$$

Eliminating the time $t$ between (2) and (3) gives

$$\dot{x} = \frac{\sqrt{\frac{x^2}{c^2} + \frac{2xm}{Ee}}}{\frac{x}{c^2} + \frac{m}{Ee}}. \tag{4}$$

Suppose the electron to move in an alternating electric field of amplitude $E_1$, and frequency $\omega/2\pi$. The effects upon the motion due to radiation from the field and the electron are neglected. Letting the subscript 1 denote the alternating potential case, the equation of motion of the electron is

$$\ddot{x}_1 = E_1\frac{e}{m}\left(1 - \frac{\dot{x}_1^2}{c^2}\right)^{3/2}\cos \omega t. \tag{5}$$

With initial conditions $t = x_1 = \dot{x}_1 = 0$, the solution of (5) is

$$\dot{x}_1 = \frac{\frac{E_1ec}{m\omega}\sin \omega t}{\sqrt{c^2 + \frac{E_1^2e^2}{m^2\omega^2}\sin^2 \omega t}} \tag{6}$$

and

$$x = \frac{c}{\omega}\left[\cos^{-1}(\alpha \cos \omega t) - \cos^{-1}\alpha\right], \tag{7}$$

where

$$\alpha = \frac{\frac{E_1 e}{m}}{\sqrt{\frac{E_1^2 e^2}{m^2} + \omega^2 c^2}}. \tag{8}$$

Eliminating $t$ between (6) and (7) gives

$$\dot{x}_1 = c\,\frac{\sqrt{\alpha^2 - \cos^2\left(\frac{\omega x_1}{c} + \cos^{-1}\alpha\right)}}{\sin\left(\frac{\omega x_1}{c} + \cos^{-1}\alpha\right)}. \tag{9}$$

When $E$ and $E_1$ are the potentials just sufficient to set up luminosity we may equate (4) and (9).

This leads to

$$\frac{\sqrt{\frac{x^2}{c^2} + \frac{2xm}{Ee}}}{\frac{x}{c^2} + \frac{m}{Ee}} = c\,\frac{\sqrt{\alpha^2 - \cos^2\left(\frac{\omega x_1}{c} + \cos^{-1}\alpha\right)}}{\sin\left(\frac{\omega x_1}{c} + \cos^{-1}\alpha\right)}. \tag{10}$$

Where $\alpha$ is given by (8), and $x$ and $x_1$ are now the distances the electron travels before it attains the critical velocity for the direct and alternating potential cases, respectively. When $\omega = 0$ (10) becomes an identity. Further, if $e/m$ refers to the charged atom or molecule and not to the electron, the variation of mass with velocity may be neglected, and (10) simplifies to

$$E_1 x_1 - Ex = \frac{x_1^2 \omega^2 m}{2e}. \tag{11}$$

We now make use of the experimental fact that within the error of experiment $E$ was equal to $E_1$ for all the cases examined. The following numerical values were chosen: $e/m = 1.77 \times 10^7$ for the electron, $\omega = 10^7$, $x = x_1 = 1$, and $c = 3 \times 10^{10}$. $x$ and $x_1$ were unknown, but since they could not be greater than the distance between the electrodes we have taken them to be of the order of one centimeter. Their exact values are of little importance in the calculations from (10). When these values are substituted in (10) it is found that $E_1$ is greater than $E$ by a quantity of the order of magnitude of one thousandth part of a volt, and that not until $\omega x_1$ becomes as large as $c$ does $E\delta$ differ appreciably from

$E_1$. This is in accord with the experimental results. If we chose the value of $e/m$ for the hydrogen molecule, *i.e.*, $0.5 \times 10^4$, $\omega = 10^7$, $x = x_1 = 1$, and $c = 3 \times 10^{10}$, upon substitution in (11) we find $E_1 - E =$ 100 volts and for the oxygen molecule $E_1 - E = 1600$ volts. Of course it is not permissible to use $x = x_1$ in (11), but since $x_1$ must always be greater than $x$ the values of $E_1 - E$ just given are minimum values. Further it is seen from (11) that $E_1 x_1 - Ex$ increases with $\omega^2$. These results are clearly at variance with the experimental results. We therefore conclude that the charged particle which collides with the gaseous molecule, thereby originating the luminosity in the gas, is the electron. After luminosity has once set in subsequent ionization is caused by both electrons and charged molecules or atoms as J. J. Thomson and others have shown.

## THE RADIO FREQUENCY FLASHES.

In order to determine whether the luminosity of a gas stimulated by radio frequency current flickered at a radio frequency the discharge tube *d*, Fig. 2, excited by damped-wave radio frequency current was pointed at a mirror *m*, 3 cms. square, about four meters distant, which rotated 12,000 times per minute. The light reflected from the mirror was observed in a low-power telescope *h*. Fig. 2 shows the arrangement. The 25,000 volt transformer *p* charged the condenser *c* which discharged through the coil *b*, the tube *d*, the hot-wire ammeter *a*, and the spark gap *g*. When the mirror was rotated the flashes from the tube were seen

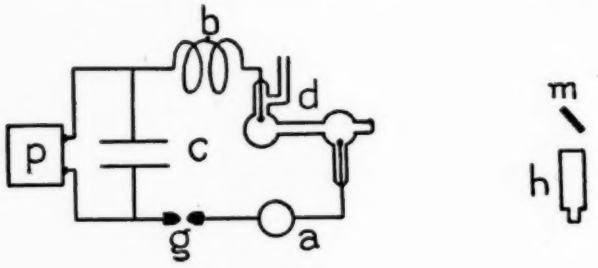



Fig. 2.

spread out into streaks of light. Each streak consisted of a series of separate flashes occurring at the frequency of the radio frequency current through the gas. The general appearance is sketched in Fig. 3. Observations on hydrogen, oxygen, air, and argon showed that the radio frequency striations were discernable for frequencies as high as $10^6$, but for frequencies greater than this the streak appeared continuous. The shortness of the time of a dark striation is worthy of remark. For example, in the case of hydrogen at 3 mm. pressure a frequency of $0.86 \times$

$10^6$ produced dark striations whose length and intensity were perhaps one tenth of the length and intensity of a bright striation. Thus in $6 \times 10^{-8}$ seconds the intensity of the gas passed from a high value to a low one and back to a high value again. The fact that there was an upper limit of frequency above which no striations could be seen was due in part to the limitations of the apparatus, and in part to the greater damping of the oscillations at the higher frequencies as shown by the shortness of the streak and the logarithmic decrement of the circuit. The non-appearance of the dark striations may also have been caused by the persistence of the luminosity, for W. Wien[1] and G. Mie[2] have shown in the case of the light from canal rays of hydrogen and oxygen

Fig. 3.

that the time for the luminosity to decrease to $1/e\delta$th of its value was of the order of $10^{-8}$ seconds.

With hydrogen or argon in the discharge tube the first one or two flashes of a radio frequency series, such as pictured in Fig. 3, were nearly white, the next few flashes pink, and the last flashes red. The cause of this was attributed to the energy distribution in the visible spectrum of the gas. In the case of hydrogen the condenser discharge brought out the Balmer lines strongly with the secondary spectrum relatively weak. The first few flashes owed their whiter color to the predominance of $H_\beta$ and $H_\gamma$ caused by the relatively great intensity of the first few oscillatory discharges of the condenser. As the discharges become less violent $H_\alpha$ became more prominent and colored the later flashes red.

STATE UNIVERSITY OF IOWA,
March, 1922.

[1] Ann. d. Phys., 66, 229, 1921.
[2] Ann. d. Phys., 66, 237, 1921.

# THE EFFECT OF THE MAGNETIC FIELD ON THE ABSORPTION OF X-RAYS.

BY JOSEPH A. BECKER.

SYNOPSIS.

*Effect of a magnetic field on the absorption of x-rays*, if it can be measured, would have an important bearing on the theory of atomic structure. Since the effect is very small, a differential method was adopted and by eliminating various spurious effects the apparatus was made sensitive enough to detect a change of 1 part in 10,000. Observations were made with a peak voltage of 80 kv. across the Coolidge tube (mean wave-length about 0.3 Å.) and with a magnetic field $H$ of about 18,000 gauss. For $H$ perpendicular to the rays, *aluminum, carbon, copper, iron, nickel, platinum, zinc, and silver* showed changes in absorption coefficients of $+8 \pm 6$, $-5.6 \pm 2$, $+0.8 \pm 0.4$, $-10 \pm 2$, $+1.6 \pm 0.5$, $+1.7 \pm 0.4$, $-1.2 \pm 0.4$ and $+1.6 \pm 0.8$ parts in 10,000 respectively, while with $H$ parallel to the rays the corresponding changes were $+2.7 \pm 1$, $+3 \pm 1$, $+1.4 \pm 1$, $-0.5 \pm 2$, $+0.7 \pm 2$, $+1.1 \pm 1$ and $+1.3 \pm 1 \times 10^{-4}$, silver not being tried. These results are in accord with the hypothesis that the magnetic properties are largely determined by the outer shell or valency electrons, since at the wave-lengths used by far the greater part of the absorption is due to the inner electrons. Wood was also tested with softer rays having a mean wave-length of about 1.2 Å., and showed a change of $+80 \pm 20 \times 10^{-4}$ as compared with $3 \times 10^{-4}$ for carbon for wave-length 0.3 Å. Following the suggestion of this result it is proposed to do further work with light elements and softer x-rays.

*Differential Method of Measuring Small Changes of Intensity of an X-ray Beam.*—The apparatus, which includes two similar ionization chambers connected so that the ionization currents nearly neutralize each other, is described in detail together with the precautions necessary to eliminate various sources of error and to attain the sensitivity mentioned above.

*Bumstead Electroscope.—A simple type* is described. Care should be taken to eliminate convection currents within the instrument.

THE following investigation was undertaken because of the conviction that the structure of the atom cannot be satisfactorily explained without taking into account magnetic forces. It was hoped that an applied magnetic field would orient the ultimate magnetic particle and that this shifting would result in a measurable change in the absorption of x-rays. A study of this effect would throw a new light on the nature of the ultimate magnetic particle and on its function in the atom.

This search is not new. In 1914 and 1916 Dr. Forman[1] sought for this effect in iron. In his second paper he reports an increase in absorption of five to seven parts in a thousand when iron is magnetized in a direction parallel to the x-ray beam. Soon thereafter A. H. Compton[2]

[1] PHYS. REV., *3*, 306–313, 1914 and *7*, 119–124, 1916.

[2] J. Wash. Acad. Sci. *8*, 1, 1918 and PHYS. REV., *14*, 20–43 and 247–259, 1919.

developed his theory of scattering and later stated "that the effect observed by Forman is of the order of magnitude to be expected if the electrons are rings of electricity which are oriented by the magnetic field."[1] This led him to look for a change in $\gamma$-ray absorption in magnetized and unmagnetized iron. He reports negative results of $.023 \pm .018$ and $.004 \pm .019$.[3]

Since 1916 our knowledge of x-ray production and absorption, as well as the technique of control and measurement, has advanced sufficiently to warrant a repetition of Forman's work as well as an extension to other materials than iron.

## APPARATUS.

The method used is essentially a differential one and is necessarily so because the changes sought are small.

The general arrangement of apparatus was much the same as that used by Forman. A radiation-type, tungsten-target Coolidge tube, $T$,[2] is practically completely enclosed in a lead box $L$, Fig. 1, and sends two

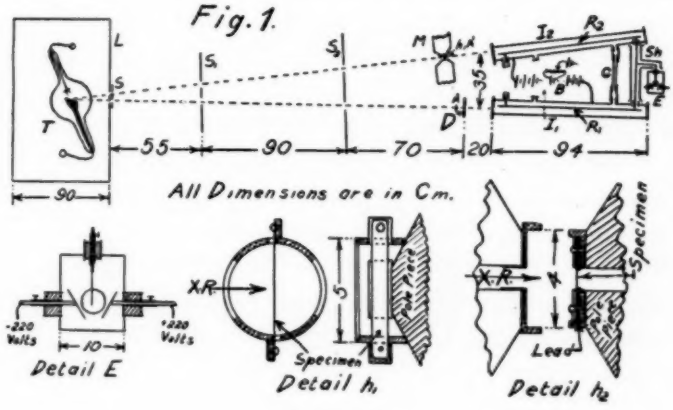



Fig. 1.

beams of x-rays through three pairs of preliminary lead slits, through the absorbers $A$ and $A'$, and into two identical ionization chambers $I_1$ and $I_2$. The rods $R_1$ and $R_2$ are connected together and to the leaf of a Bumstead electroscope $E$.[3] This system can be earthed by means of a mercury-break key, and is shielded from electrostatic disturbances by a tin shield $Sh$. The casings of the ionization chambers, as well as the movable plates of the electroscope, are connected to the terminals of a 420-volt battery of dry cells, $B$, whose middle point is earthed. $G$ is a

[1] PHYS. REV., *17*, 38–41, 1921.

[2] Very kindly placed at the disposal of Prof. Richtmyer by Dr. Coolidge.

[3] Am. J. of Sci., *32*, 405–406, 1911 and Phil. Mag., *22*, 910, 1911.

glass tube connecting the two chambers. $M$ is a powerful electromagnet of Swiss type. The diameter of the face of the pole-pieces was 2 cm. in the first part of the investigation and 4 cm. in the second part. $h$ is a holder to be described in detail later. $D$ is a rectangular opening of lead, the upper edge of which is attached to a slow motion screw.

The procedure is as follows: one specimen is placed between the pole-pieces, while an exactly similar one is placed in front of $D$. The size of the slit at $D$ is varied until practically no net charge accumulates on the rods $R_1R_2$ and the leaf shows either a small rate of drift or none at all. The magnet is energized. If the absorption of the specimen in the field is increased, the ionization in $I_2$ will decrease, and the leaf will show a change in the rate of drift ($\Delta\delta$) where $\delta$ is the rate of drift in divisions per minute. By subsequently determining how much the height of the slit at $D$ must be increased to produce the same $\Delta\delta$ we can compute $\Delta I/I$, the proportional change in the intensity of the transmitted beam. Then by means of a formula to be developed later we can compute $\Delta\mu/\mu$, the proportional change in the absorption coefficient due to the field $H$.

Since the effect is small it is necessary to be able to keep the two ionization currents balanced to within 1 or 2 parts in 10,000. Consequently every effort was made to reduce the errors to a minimum. The larger part of the time was taken up in determining and eliminating spurious changes in $\delta$. The following list gives the chief factors to be guarded against.

### Sources of Error.

(*a*) Electrostatic effects.
(*b*) Unsteadiness of leaf of electroscope.
(*c*) High-resistance leaks.
(*d*) Stray x-radiation.
(*e*) Slight changes in the position of the focal spot.
(*f*) Changes of current through the tube.
(*g*) Peculiarities of the ionization chambers.
(*h*) Effect of the magnetic field on the tube or ionization chambers.
(*i*) Movement of the specimen caused by $H$ or by the slight shifting of the pole-pieces.

To show how these errors were eliminated it is necessary to give a detailed description of the apparatus.

### The Electroscope.

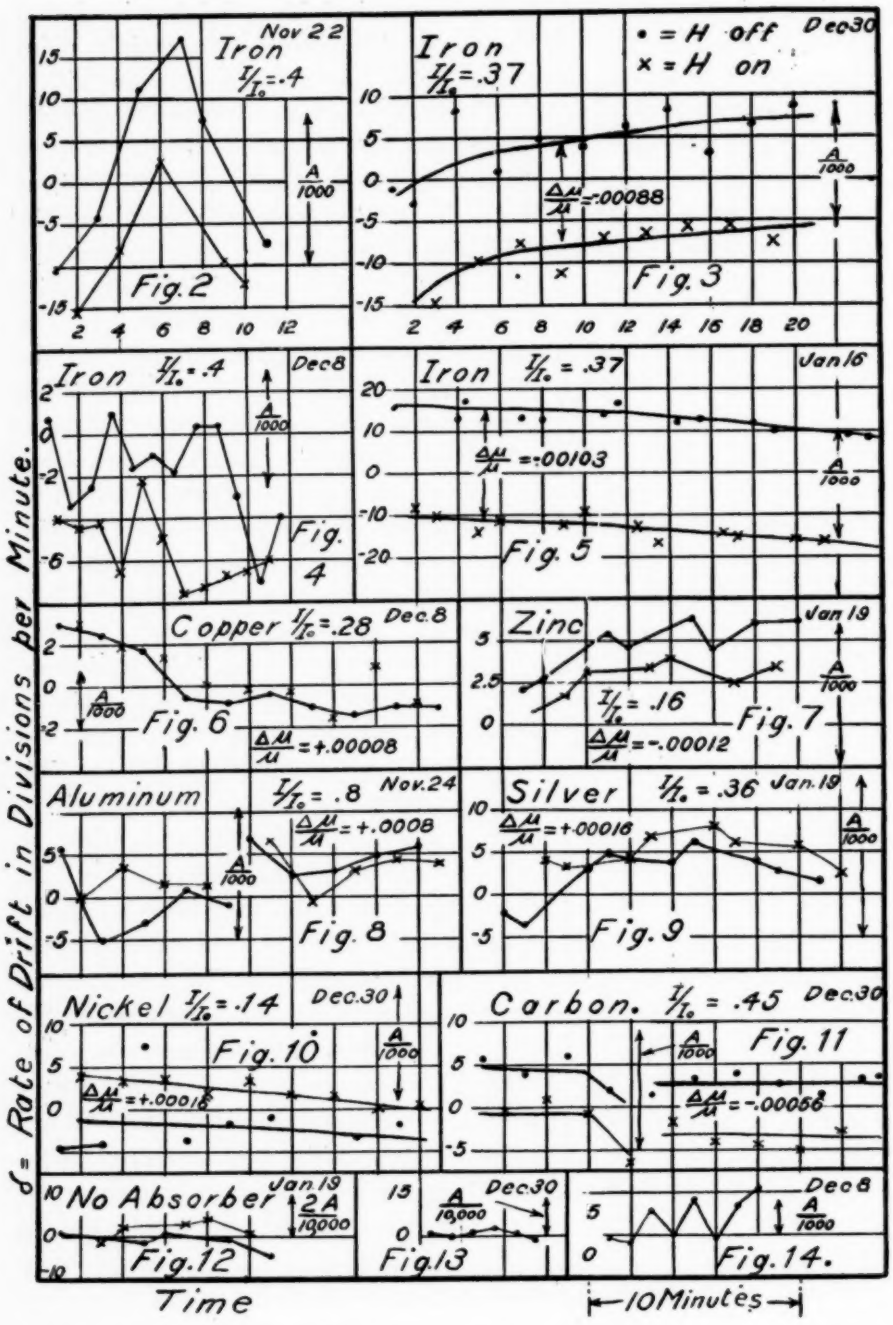
Fig. 1 shows a detail drawing of the electroscope. It can be constructed by an amateur mechanic in a short time. The brass box was made detachable, but the joints were sealed with wax to make them

air tight. The plates and the leaf are adjustable. Sulphur insulation was found convenient and satisfactory. The position of a definite point on the gold-leaf was observed through a low-power microscope with a 50-division scale in the ocular. These 50 divisions correspond to approximately 2 mm. At first considerable difficulty was encountered in keeping the grounded leaf at rest. The trouble was finally ascribed to heat convection currents, and was eliminated by completely enclosing the instrument with a cardboard housing. The working sensitivity of the leaf was about 80 div. per volt on the leaf. This sensitivity could easily have been increased four or five fold by either lowering the leaf, moving both plates closer, or by increasing the voltage on the plates.[1] At the high sensitivities it becomes somewhat more difficult to keep the position of the leaf steady. Unsymmetrical changes of voltage on the plates were about one fifth as effective in deflecting the leaf as the same voltage on the leaf, *e.g.*, if the ground is shifted one volt the resultant deflection is the same as if the leaf had been charged to .2 volt. This fact necessitated keeping the relative voltages on the plates constant to within 10 millivolts. When not too old, the dry cells proved satisfactory so long as their temperature was kept constant.

The drift in the leaf due to change of plate voltage, high resistance leaks, and electrostatic disturbances was seldom more than 5 divisions in half an hour. Neither was the rate of drift increased by running the x-ray tube with the openings at $h$ and $D$ closed by small lead plates. This shows that the first four sources of error mentioned above were effectively eliminated. To accomplish this it was found essential completely to inclose the tube with lead and put up the preliminary screens.

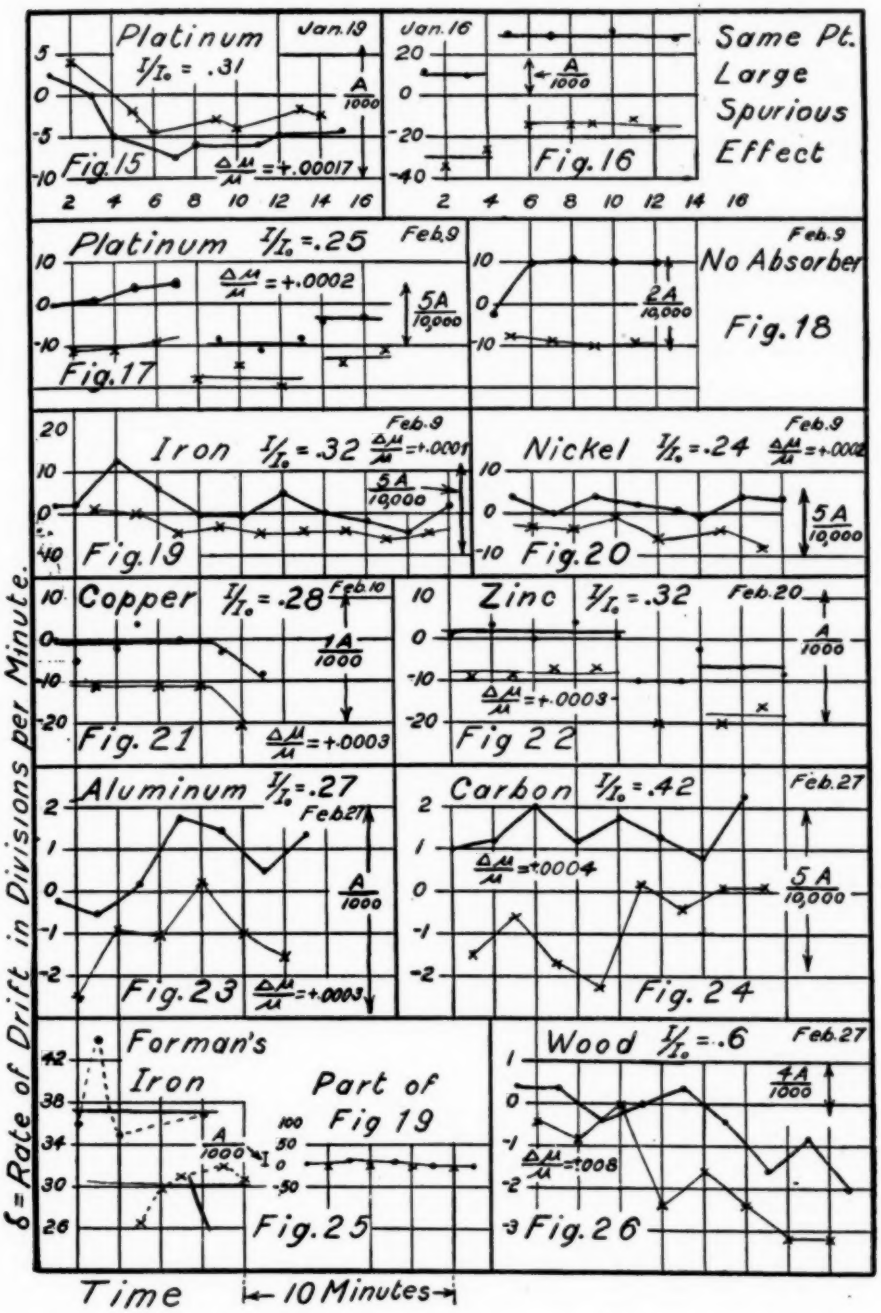
Sources of error $e$, $f$, and $g$ were found by repeatedly observing that $\delta$ would change radically whenever the current through the tube changed. At this time the high tension for the tube was furnished by a G. E. x-ray transformer while the filament was supplied from a step-down transformer. Even though the primary of both transformers was supplied from a rotary converter (D.C. to A.C.) whose voltage could be kept constant to within 2 per cent., yet the current through the tube would vary as much as 50 per cent. Ideally this should not have disturbed a balance since both beams should be affected equally. Practically it did and the only satisfactory way of keeping the current steady was to light the filament by means of a 12-volt storage battery in the high-tension circuit. The filament current was varied by means of a slide-resistance operated by an insulated handle. Even with this arrangement the contacts in the filament circuit were gone over periodically to insure steady currents.

[1] Dadourian, PHYS. REV., 14, 238, 1919, obtained a working sensitivity of 5,000 divisions per volt.


Iron Nov 22 I/I₀=.4 Fig. 2
Iron I/I₀=.37 • = H off × = H on Dec 30 Δμ/μ=.00088 Fig. 3
Iron I/I₀=.4 Dec 8 Fig. 4
Iron I/I₀=.37 Jan 16 Δμ/μ=.00103 Fig. 5
Copper I/I₀=.28 Dec. 8 Δμ/μ=+.00008 Fig. 6
Zinc Jan 19 I/I₀=.16 Δμ/μ=-.00012 Fig. 7
Aluminum I/I₀=.8 Nov. 24 Δμ/μ=+.0008 Fig. 8
Silver I/I₀=.36 Jan. 19 Δμ/μ=+.00016 Fig. 9
Nickel I/I₀=.14 Dec. 30 Δμ/μ=+.00018 Fig. 10
Carbon. I/I₀=.45 Dec. 30 Δμ/μ=-.00056 Fig. 11
No Absorber Jan 19 Fig. 12
Dec. 30 Fig. 13
Dec 8 Fig. 14.
δ = Rate of Drift in Divisions per Minute.
Time
10 Minutes

In all Figs. the values of $\delta$ for $H$ off are represented by $\cdot$; for $H$ on, by an $x$. $H$ = approx. 18,000 gauss.

In Figs. 2 to 16, $H$ was perpendicular to the x-rays; the voltage was 80 kv. peak; a $+\Delta\delta$ means a decrease in $I$, or an increase in $\mu$.




In Figs. 17 to 24, $H$ was parallel to $X$; the voltage was 80 kv. peak; a $+\Delta\delta$ means an increase in $I$ or a decrease in $\mu$.

In Fig. 26, $H$ was parallel to $X$; the voltage was 27 kv. peak; a $+\Delta\delta$ means a decrease in $\mu$.

A pin-hole picture of the focal spot showed that it consisted of a ring 7/16 inch in diameter with two irregular small areas inside. Consequently if the first slit $S$ is narrow and the focal spot for any reason shifts, even though the shift is so slight as to be imperceptible, a slightly different area becomes effective in illuminating the slit at $D$ and thus the balance is destroyed. The preliminary slits were therefore made 3/4 inch wide while the final slits at $D$ and $h$ were only 1/8 to 1/4 inch wide. In this way every point of the final slit received radiation from every point of the focal spot even though the focal spot did shift slightly. Incidentally, widening the preliminary slits also increased the available energy. The improvement brought about by this change shows up clearly by contrasting the steadiness in Figs. 2 and 14 for narrow slits with Figs. 3 and 13 for the widened slits.

The ionization chambers were made of brass tubing and were fitted with square ends. They were mounted on sulphur supports. The rods were supported and insulated by sulphur plugs containing the usual earthed guard rings. The chambers were filled with methyl bromide. Unfortunately this gas in the presence of moisture reacts with zinc and copper thus making it necessary to refill the chambers every three or four weeks. When doing so, care was taken to fill both chambers to the same pressure, otherwise a change in the tube current of .1 milliamp might unbalance the ionization in the chambers by several parts in 1,000. Later the two chambers were connected by a glass tube.

During the course of the investigation it was noticed that the balance was particularly sensitive to slight shifts in the rear end of the ionization chambers. A further study revealed the fact that an appreciable percentage of the ionization was caused by photoelectrons emitted by the rear end of the chamber. Materials of low atomic weight were found to cause a smaller increase in the ionization than those of high atomic weight. The arrangement decided upon as least troublesome was an aluminum plate coated on the inside with wax.

## Spurious Effects Due to the Magnetic Field $H$.

Forman found that the stray field of his electromagnet deflected the electron stream in his tube. He finally remedied the difficulty by means of compensating coils and iron screens. The magnet in this present investigation was placed at a considerable distance from the tube. Its stray field near the tube was less than the earth's field and when possible was opposed to it. The final test as to whether the stray magnetic field affects either the tube or the ionization is to make blank runs either with no absorbers or with absorbers in front of the magnet. Several

such runs were made and in no case was any effect greater than 2 parts in 10,000 obtained. (See Fig. 18).

Several times large apparent changes in absorption were noted when the specimen was between the pole-pieces, but in all such cases it could be shown that either the field distorted the specimen or the shifting of the pole-pieces displaced the specimen. This was particularly true in the case of iron and nickel, and with thin specimens. Fig. 16 shows a spurious change of about 2½ parts in 1,000. Due to the high absorption coefficient for platinum the specimen was only 1 or 2 mils thick. Small forces might easily distort the thin specimen. When this same specimen was pasted on a thin uniform strip of wood and another run taken, as shown in Fig. 15, $\Delta I$ is only a few parts in 10,000. Practically the same result was obtained when the specimen was tightly clamped in the holder.

## The Specimen Holders.

Two holders $h_1$ and $h_2$ were designed and are shown in detail in Fig. 1. $h_1$, which was used when $H$ was perpendicular to the rays, consists of a brass collar with bevelled edges which match the pole-pieces. Two screws fasten the specimen to two ledges at opposite ends of a diameter. Perpendicular to this diameter are openings to allow the beam to pass. This holder may not be as reliable as the accuracy of the remainder of the outfit warrants. Consequently a new one has been designed which, it is hoped, will give more reliable results.

Holder $h_2$ was carefully designed and constructed. It was used when $H$ was parallel to the rays. The specimen is firmly held in front of the lead opening by means of screws passing through the brass cover. The pole-pieces are firmly screwed up against the holder.

## The Final Slit at $D$.

The opening at $D$ was usually 3/16 inch wide and about 1/2 inch high. A balance was obtained by changing the height by means of the micrometer screw. One turn corresponds to 1/100 inch and there are 100 divisions on the drum. Thus with a slit 1/2 inch high, 5 drum divisions ($5D$) correspond to a change in area of 1 part in 1,000, *i.e.*, $A/1{,}000$. By noting $\delta$ for a series of positions of the drum, $\Delta\delta$ for $10D$, or else $\Delta\delta$ for $A/1{,}000$ can be computed. The uniformity of intensity of the x-ray beam over the whole opening was shown by the fact that this ratio was independent of the height of the opening.

In all measurements of large rates of drift, say greater than 60 divisions per minute, it was found necessary, in order to get consistent results, to apply a correction to the observed $\delta$. Table I. gives the values of the

corrections to be added to the absolute value of the observed $\delta$. These corrections were obtained by noting $\delta$ for a number of openings differing by equal small steps and plotting $\delta$ against the opening. Instead of a straight line, a curve was obtained which deviated more and more from the straight line as $\delta$ increased. The deviations gave the corrections to be added. This lag is probably due to air friction and is a function of the dimensions and shape of the leaf and the air pressure. It is analogous to the lag in a quadrant electrometer.

TABLE I.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Observed $\delta$..... | 50 | 100 | 150 | 200 | 250 | 300 | 400 |
| Correction..... | .5 | 2.5 | 9 | 19 | 37 | 60 | 90 |

SENSITIVITY OF APPARATUS.

To show how sensitive the apparatus is, one need only obtain a balance, and then interpose a very thin sheet of paper. After a few seconds' lag the leaf begins to drift and continues to do so until a few seconds after the paper is removed. A few degrees change in temperature in the slit $D$ can be detected; the slight "give" in the floors caused by a person walking past the supports for the slit $D$ produces an observable effect; air currents also cause disturbances. Under these circumstances it seems almost hopeless to try to measure an effect less than one part in 1,000 with an accuracy better than 10 per cent. However, if the temperature and current could be maintained constant and if mechanical disturbances were minimized, the apparatus could detect changes as small as 2 or 3 parts in 100,000.

COURSE OF A COMPLETE RUN.

The following illustrates the course of a complete run.

Voltage across tube: 80 kv. peak.

Sensitivity of leaf: 44.2 div./volt.

1. Steady test: x-rays shut off by lead plates. Position of leaf every 15 seconds:

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 25.2 | 25.2 | 25.0 | 25.0 | 24.9 | 24.9 | 24.9 | 24.8 | 24.8 | 24.8 | 24.7 | 24.7 |
| 24.7 | 24.5 | 24.4 | 24.2 | 24.2 | 24.2 | 24.2 | 24.2 | 24.1 | 24.0 | 24.0 | 24.0 |
| 24.0 | 24.0 | 23.9 | 23.8 | 23.9 | 23.9 | 23.9 | 23.8 | 23.7 | 23.6 | 23.6 | 23.7 |
| 23.7 | 23.7 | 23.7 | 23.6 | | | | | | | | |

2. Sensitivity determination with no absorber in.

Size of opening = 3,900 drum divisions or 3,900 $D$,

Drum scale 20 up $\delta = -40 \times 60/11.4 = -210$ Corrected $\delta = -230$,
Drum scale 25 up $\delta = -23.3 \times 60/30 = -46.6$ Corrected $\delta = -47$,
Drum scale 30 up $\delta = 40 \times 60/18.9 = 127$ Corrected $\delta = +131$,

$\Delta\delta/10D = 180 \times 2 = 360$ for 2.2 milliamps = 82 per milliamp,

$\Delta\delta$ for $A/1000 = \Delta\delta/10D \times 3.9/10 = 140$.

3. Steady test with x-rays entering chambers. Readings of leaf every 15 seconds:

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 19.0 | 19.5 | 18.5 | 19.5 | 20.0 | 20.7 | 19.5 | 18.5 | 19.7 | 21.0 | 22.0 | 21.0 |
| 21.0 | 21.5 | 21.8 | 22.5 | 24.0 | 23.8 | 24.0 | 25.0 | 25.3 | 25.0 | 24.0 | 24.0 |

4. Sensitivity with iron absorber in. Opening: $3800D$.

Drum 40 up $\delta = -40 \times 60/15 = -160$ Corrected $\delta = -170$,
Drum 60 up $\delta = -20 \times 60/13 = -92$ Corrected $\delta = -94$,
Drum 80 up $\delta = -12$ Corrected $\delta = -12$,

$\Delta\delta/10D = (76 + 82)/2 \times 2 = 39.5$ for 1.3 milliamps = 30.4 per milliamp,

$$I/I_0 = \frac{\Delta\delta/10D \text{ for Fe absorber}}{\Delta\delta/10D \text{ for no absorber}} = 30.4/82 = .37,$$

$$\Delta\delta \text{ for } A/1000 = (39.5/10) \times 3.8 = 15.$$

5. Effect of magnetic field on absorption of iron. $H = 18{,}000$ gauss. $H$ is put on for one minute every other minute starting with the second. The position of the leaf is read every 15 seconds.

| $H$ Off | | | | | $H$ On | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Switch closed | | | | Switch opened |
| 33.0 | 32.8 | 33.0 | 34.0 | 33.0 | 31.5 | 29.2 | 25.5 | 24.5 |
| | 26.0 | 28.0 | 29.7 | 30.8 | 29.0 | 26.0 | 25.0 | 24.8 |
| | 26.2 | 30.0 | 31.2 | 34.0 | 32.5 | 30.0 | 28.3 | 28.5 |
| | 28.8 | 29.5 | 30.5 | 30.5 | 29.5 | 29.0 | 27.5 | 30.0 |
| | 31.0 | 34.0 | 35.8 | 36.5 | 34.0 | 32.0 | 30.0 | 29.0 |
| | 31.0 | 33.0 | 35.5 | 38.0 | | | | |

A positive $\Delta\delta$ means an increase in absorption, or a decrease in $I$.

From this data the average $\delta$ for each minute was computed and plotted in the latter half of Fig. 3.

This figure shows a change of $\delta$ due to $H$ equal to $-13$ div. Since $\Delta\delta$ for $A/1000 = 15$;

$$\frac{\Delta I}{I} = -\frac{-13}{15 \times 1000} = +\frac{8.7}{10{,}000}.$$

From a formula developed below

$$\frac{\Delta\mu}{\mu} = -\frac{1}{\log_e(I_0/I)} \cdot \frac{\Delta I}{I} = -1.005\frac{+8.7}{10{,}000} = \frac{-8.8}{10{,}000}.$$

Consequently a field of 18,000 gauss decreases the absorption coefficient of iron by 8.8 parts in 10,000.

## DEVELOPMENT OF FORMULÆ.

As is well known,

$$I = I_0 e^{-\mu t}. \tag{1}$$

If $\mu$ can be made to change in a given specimen, then

$$\frac{dI}{d\mu} = -tI_0 e^{-\mu t} = \frac{\Delta I}{\Delta \mu} = -tI \tag{2}$$

or

$$\frac{\Delta I}{I} = -t\Delta\mu.$$

From (1)

$$t = \frac{\log(I_0/I)}{\mu}; \quad \therefore \frac{\Delta I}{I} = -\frac{\Delta\mu}{\mu} \times \log\left(\frac{I_0}{I}\right)$$

or

$$\frac{\Delta\mu}{\mu} = -\frac{1}{\log\,(I_0/I)} \cdot \frac{\Delta I}{I}. \tag{3}$$

Given: $I_0$, $\mu$, and $\Delta\mu$ for a certain material. What is the best thickness to use so that $\Delta I$ shall be a maximum?

From (2)

$$\Delta I = -I_0 t e^{-\mu t}\Delta\mu$$

For a maximum

$$\frac{d(\Delta I)}{dt} = 0$$

or

$$-I_0\Delta\mu(e^{-\mu t} - \mu t e^{-\mu t}) = 0$$

Since $I_0$, $\Delta\mu$, and $e^{-\mu t}$ are not zero,

$$1 - \mu t = 0 \qquad \text{or} \qquad \mu t = 1$$

or

$$\log_e I_0/I = 1, \qquad I_0/I = 2.73; \qquad I/I_0 = .368.$$

That is $\Delta I$, which determines $\Delta\delta$, will be greatest if $t$ is so chosen that $I/I_0 = .368$.

## RESULTS.

Figs. 2–16 show the results obtained with $H$ perpendicular to the path of the x-rays; Figs. 17–26, the results for $H$ parallel to the x-rays. For all but the last two figures the peak voltage across the tube was about 80 kilovolts, which corresponds to a minimum wave-length of .15 Å. The maximum energy was probably in the neighborhood of .3 Å. Each figure contains the date on which the data were obtained, the values of

$\Delta I/I$, $\Delta\mu/\mu$, and $\Delta\delta$ for $A/1000$. It is important to take this last-named factor into account when comparing the curves.

A comparison of the steadiness of this apparatus with that attained by Forman is given in Fig. 25 which shows Forman's results for iron with 81 kv. (R.M.S.) across the tube, and the present result for iron under similar conditions, both plotted to practically the same scale.

Figure 26 shows one of two preliminary runs with a peak voltage of 27 kv. across the tube. A previous run on wood at the higher voltage had revealed a $\Delta\mu/\mu$ of 4 or 5 parts in 10,000. At the lower voltage the sensitivity, consistency, and reliability are considerably less but still $\Delta\mu/\mu$ is clearly about 8 parts in 1,000 or about 16 times as large as before. This would indicate that larger changes may reasonably be looked for at longer wave-lengths with low atomic weight elements. This clue, it is hoped, can be followed up in the next few months.

The results show that while the magnetic field does change the absorption of x-rays in various materials the effects for wave-lengths near .3 Å. are small. At this wave-length the largest effect is shown by iron for which $\Delta\mu/\mu$ is about 1 part in 1,000 when $H$ is perpendicular[1] to $X$. For $H$ parallel to $X$, Fig. 19 shows that the change is much smaller,[1] which may be partly due to the large demagnetizing field for such a thin sheet of iron. Of the other materials examined carbon and aluminum show the largest change. Nickel, platinum, copper, zinc and silver show changes smaller than 3 parts in 10,000 for either direction of $H$. At a mean wave-length in the neighborhood of 1.2 Å., wood shows a change in absorption of about 8 parts in 1,000 for $H$ parallel to x-rays.

The following list sums up the values of $\Delta\mu/\mu$[2] together with an estimated probable error. The conditions under which each value was obtained can be found in the figures or in the legend for the figures. The estimate of the probable error is based on the oscillations of $\delta$, the value of $\Delta I/I$ due to $H$ for no absorber, and on the author's experience and judgment of the likelihood of small spurious effects.

All results are expressed in number of parts change in 10,000, a plus sign meaning an increase in $\mu$.

For $H$ perpendicular to $X$ rays:

| | | |
|---|---|---|
| Iron $-10 \pm 2$, | Nickel $+1.6 \pm 0.5$, | Platinum $+1.7 \pm 0.4$, |
| Copper $+0.8 \pm 0.4$ | Zinc $-1.2 \pm 0.4$, | Silver $+1.6 \pm 0.8$, |
| Carbon $-5.6 \pm 2$, | Aluminum $+8 \pm 6$. | |

[1] Opposite to Forman's results.

[2] Corrected for a small effect observed with no absorber, which was never greater than 2 parts in 10,000.

For $H$ parallel to $X$ rays:

| | | |
|---|---|---|
| Iron $-0.5 \pm 2$, | Nickel $+0.7 \pm 2$, | Platinum $+1.1 \pm 1$, |
| Copper $+1.4 \pm 1$, | Zinc $+1.3 \pm 1$, | Carbon $+3 \pm 1$, |
| Aluminum $+2.7 \pm 1$, | Wood (longer wave-lengths) $+80 \pm 20$. | |

## Discussion of Results.

These results are in accord with the hypothesis that magnetic properties are largely conditioned by the outer atomic shell or valency electrons. If the magnetic fields inside the atom are actually as large as is supposed, we cannot hope to penetrate deeply into the atom with external fields. Consequently we should hardly expect to produce any changes in the inner shells. Now it is generally believed that the K absorption and emission are associated with the innermost shell while the L and M radiations are due to the next two shells of electrons respectively. Professor Richtmyer[1] has shown that very probably for wave-lengths less than the $K_a$ limit, by far the larger part of the absorption is used up in exciting the K fluorescent radiation, a small percentage of the energy absorbed, for example, let us say 5 per cent., excites the L fluorescence, and presumably even a much smaller percentage, let us say .5 per cent., goes to excite the M fluorescence. On the above hypothesis we should expect to be unable to affect the K and L absorption of all substances having three or more shells of electrons. To be specific, let us consider aluminum which on Langmuir's theory contains a K shell of 2 electrons, an L shell of 8 electrons, and an outer shell of 3 electrons. If the external magnetic field produces no change in the K and L absorption but as much as a 10 per cent. change in the absorption due to the outer shell, the change in the total absorption would amount to only $.10 \times .005$ or 5 parts in 10,000. On the other hand, carbon which contains only 2 shells would on the same suppositions show a change in the total absorption equal to $.10 \times .05$ or 5 parts in 1,000. We should also expect a larger change in the total absorption if the wave-length were longer than the $K_a$ limit. Both of these expectations are supported by the fact that at a given wave-length carbon and aluminum show larger changes than the heavier elements (excepting possibly iron and nickel), and that wood shows larger changes at long than at short wave-lengths.

On Compton's theory of scattering we might look for an appreciable change in that part of the absorbed energy which is scattered. In the low atomic weight elements a large percentage—as much as 50 per cent.—of the absorbed energy goes into scattered radiation. This investigation shows that the change in the scattered radiation cannot exceed about 1 part in 1,000.

[1] Phys. Rev., 18, 13–30, 1921.

The most hopeful region to work in seems to lie near the absorption limit of the outermost shell. The most promising materials are the ones in the first two groups of the periodic table. While the experimental difficulties in working in the neighborhood of 100 Å. are great, the author believes that it will be well worth the effort and hopes to have the opportunity of continuing the search in that direction.

In conclusion the author wishes to express his appreciation and gratitude for the ever helpful and never failing encouragement, inspiration and assistance received from Professor Richtmyer.

CORNELL UNIVERSITY,
ITHACA, NEW YORK,
March, 1922.

# THE ACTION OF THE BOW IN STRINGED INSTRUMENTS.

BY K. C. KAR.

SYNOPSIS.

*Motion of Points of a String near the Bowing Region.*—Shadows of a small section of the horizontal string and of pins stuck in the bow were thrown on a vertical slit back of which a piece of photographic paper was moved. The resulting prints each show a saw tooth line due to the string, crossed by inclined straight lines due to the pins. Experiments were made with the bow one seventh, one tenth and one fourteenth of the length of the string from one end. In every case the speed of the points of the string is proportional to the distance from the near end. The point with a speed equal to that of the bow is called the zero point. With strong slow bowing the zero point is at the outer edge of the bow, but with lighter or faster bowing the zero point may be 2 cm. or more nearer the middle of the string. While the "wolf note" is sounding the zero point oscillates periodically with the beating; it may be stopped by increasing the pressure. The amplitude at the outer edge of the bow is proportional to the speed of the string at that point and hence will change as the zero point is shifted by variations of pressure, even when the bowing speed is constant.

## INTRODUCTION.

HELMHOLTZ, referring to the particular case in which the motion of the bowed point is represented by two step zig-zag, remarks[1] that the velocity of the string, in the forward motion "appears to be equal to that of the bow." In later treatises[2] the velocity of the forward motion is stated to be equal or about equal to that of the bow. Recently Professor Raman has made an experiment[3] with his vitrograph (see Fig. 1) and has shown that the velocity of the bow is exactly equal to the velocity of the bowed point of the string in its forward motion. His conclusion was based on the fact that the record of the pin attached to the bow and that of the string are absolutely parallel. But we should note that the photograph taken by him does not represent the motion of the bowed point, but of one a little away from it.

Now in practice a bow is never applied at a point. Thus in dealing with the problem we are to take into account the length of the bowed region, which is generally about 1 cm. long. This brings us at once to the question as to which point of the string in the bowed region, if any, has the same velocity as the bow. These problems raised by Prof.

[1] Sensations of Tone, p. 83.

[2] Lord Rayleigh's Theory of Sound, Vol. 1, and Barton's Text book of Sound, Art. 261.

[3] The Dynamical Theory of the Motion of Bowed Strings, Bulletin No. 11 of Indian Association.

Raman in his monograph[1] are solved by the following experiment made by the writer.

I am deeply indebted to Professor Raman at whose suggestion I took up the work.

## Experiment.

The apparatus is shown in Fig. 1. An arc placed in front of the apparatus provides the necessary illumination. A photographic paper contained in a dark slide is arranged to slide in grooves within the wooden box, parallel to the string. A number of pins are fixed to the bow transversely so that when bowed near the slit *S*, the images of the pins moving with the velocity of the bow, fall on the photographic paper inside the vitrograph. The transverse vibration of the string is at the same time recorded on the photographic paper. It is therefore possible by this method tog et simultaneous records of the motion of the bow and of the vibration of a point on the string in the neighborhood of the bowed region.

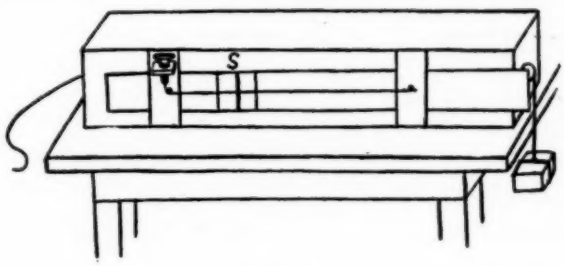



Fig. 1.

Exact determination of the point on the string whose vibrations have been recorded, is made by the following very simple method. A pin is held against the string and moved along it until its image falls on the slit. Vibrations of this point of the string have obviously been recorded. The distance of this point from one end ot the string (here it is the remoter one) is measured with a meter scale. It should be noted that the position of the arc should not be changed during the experiment.

The inner and the outer limits[2] of the bowed region are marked with ink on the string. And by moving the slit to different positions, simultaneous records of the velocity of the bow and vibrations of different points of the string are taken. The bowing pressure has been made just sufficient to elicit a steady tone with pronounced fundamental, the velocity of the bow being kept constant as far as practicable. Three sets of records have been taken for three different positions of the bow.

[1] Bulletin No. 15, Indian Association for the Cultivation of Science.

[2] The inner limit or the limit nearer the nearer end of the string.

Records obtained are somewhat like that in Fig. 2. When the slit is placed anywhere between the inner edge of the bowed region and the nearer end of the string, angle $\beta$ is always greater than angle $\alpha$ as in Fig. 2. When, however, the slit is on the other side of the bow, *i.e.*, away from the outer edge of the bowed region, $\beta$ is generally less than $\alpha$.

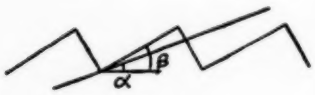



Fig. 2.

The ratios of the velocities of the string and the bow have been determined accurately from the records by measuring the tangents of the angles $\beta$ and $\alpha$ with a moving microscope (moving in two perpendicular directions) and taking their ratios.

The results of these measurements are given in the following table:—

TABLE I

Length of the string is 53.6 cm.

| | Bowed Region between. | Observed at | Vel. of String/Vel. of Bow Mean. |
|---|---|---|---|
| *A.* | 45.55 cm.–46.45 cm. | 42.1 cm. | 1.358 |
| | | 43.65 " | 1.133 |
| | | 47.40 " | .667 |
| | | 49.20 " | .484 |
| *B.* | 47.65 cm.–48.55 cm. | 48.90 " | .781 |
| | | 49.40 " | .672 |
| | | 47.0 " | 1.116 |
| | | 46.5 " | 1.236 |
| *C.* | 49.3 cm.–50.25 cm. | 48.3 " | 1.273 |
| | | 48.8 " | 1.138 |
| | | 50.8 " | .565 |

## CONCLUSION.

It appears from curves (*B*) and (*C*) that the velocity of the string at the outer edge of the bowed region is the same as the velocity of the bow. But the curve (*A*) shows that the forward velocity of the string at a point away from the outer limit of the region is equal to the velocity of the bow. Thus the string in the bowed region, in this case, has smaller velocity than the

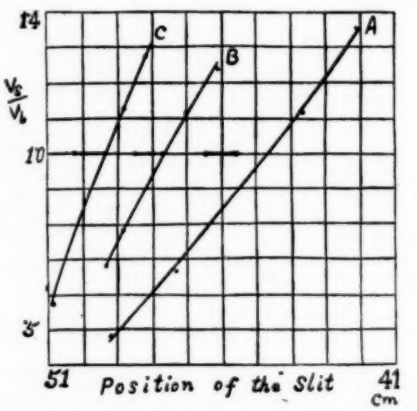



Fig. 3.

bow. The most important thing to be noted here is that the note emitted by the string is strong in the fundamental. This is shown by the photographs which are of simple Helmholtzian type of two step zig-zag. It is thus possible to get a steady fundamental when the forward velocity of the string in the bowed region is less than the velocity of the bow.

The curve (*A*) shows that the "zero point" (*i.e.*, the point which has forward velocity relative to the bow, equal to zero) is away from the outer edge of the bowed region. One would think it possible, by increasing the bowing pressure without increasing the velocity of the bow, to bring the "zero point" to the outer edge of the bowed region. This has been shown to be the case by a series of photographs, as in Fig. 4,

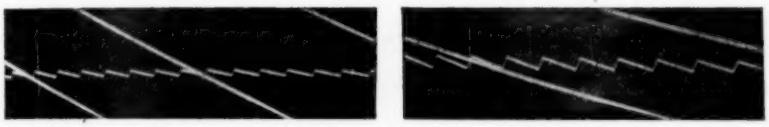


Fig. 4.

of the simultaneous motion of the bow and of a particular point of the string away from the outer edge (2 cm. from it) with different bowing pressures. When the bowing pressure is small while the velocity of the bow is great[1] the "zero point" goes away from the outer edge towards the middle point of the string and the records of the pin and the string become parallel or very nearly so. When, however, the bowing pressure is greater while the velocity is smaller or nearly the same as before the "zero point" comes nearer the outer edge and the angle between the two records appreciably increases.

Thus the "zero point" may lie anywhere within a portion of the string, one of its limits being the outer edge of the bow. The other limit for which the vibration remains two step zig-zag of the first type has not been determined. But the photographs, taken, show that it may be at a distance of about 2 cm., if not more, from the outer edge. It should be noted, further, that the effect due to any increase of bowing pressure can be counterbalanced by a corresponding increase of the velocity of the bow. Thus it will be possible to have the "zero point" away from the outer edge even with a high pressure provided the velocity of the bow is correspondingly high. If then the velocity of the bow is increased keeping the bowing pressure constant or the bowing pressure is decreased keeping the velocity constant, the "zero point" goes away from the outer edge towards the middle point of the string and the

[1] The note emitted is strong in the fundamental.

intensity of the fundamental decreases until the octave becomes most prominent. This can be easily seen in the case of the mechanical violin-player of Dr. Raman.

In the case of two-step vibrations of the first type, the amplitude of oscillation of the string at the outer edge of the bowed region is given by $(1 - a/l)Tv$, where $a$ is the distance of the point from the end and $v$ its forward velocity, $l$ being the length of the string. If the velocity of the bowed point were the same as the velocity of the bow (*i.e.*, $v$ = the velocity of the bow), as was supposed by Helmholtz and others, the amplitude of oscillation of the bowed point, *i.e.*, the intensity of the note emitted, would be independent of the bowing pressure, depending on the velocity of the bow. But it has been shown that the bowing pressure can change the value of $v$ at the outer edge even when the velocity of the bow is constant. Thus the intensity of the note emitted can be varied slightly but appreciably, simply by varying the bowing pressure.

It will appear from the curves which are approximately straight lines that the nearer the bowed region is to the end the steeper is the curve, *i.e.*, the more rapid is the change in the forward velocity per unit length of the string within and near the bowed region. Thus the portion of the string in contact with the bow during vibration will be more and more inclined to a line perpendicular to the direction of bowing. And so a greater component of the frictional force will go to produce longitudinal vibration in the string. This effect is very marked when the bow is applied near the bridge.

Let us see if the results obtained are in agreement with what follows from dynamical considerations. It is obvious that the velocity of any portion of the string within the bowed region cannot be greater than that of the bow; for in that case the frictional force will act in the opposite direction and bring down its velocity to the velocity of the bow. Further it is not possible for every element of the string in the bowed region to have the same velocity as the bow. The "zero point" therefore, cannot lie within the bowed region or between the bow and the nearer end of the string as in that case a portion or the whole of the string in contact with the bow will have velocity greater than the bow which is not possible. So the only portion in which the zero point can lie is between the outer edge and the middle point. And this is exactly what the experiment shows.

## The Wolf Note.

The results obtained throw some light on the nature of the "wolf note" [1] produced in bowed stringed instruments. It is evident from the photographs of wolf-note[2] that the inclinations of the line representing the forward motion of the string changes periodically, the period being the period of the wolf. From this it can be concluded that during the wolf the "zero point" oscillates periodically with the beating, though the pressure and velocity of the bow are constant. And it is only when, by increasing the bowing pressure, the "zero point" is fixed at the outer edge, that the wolf is controlled.

47 Corporation Street,
Calcutta,
November 14, 1921.

[1] Dr. C. V. Raman pointed out in various papers (vide "On the Wolf Note in Bowed Stringed Instruments," Phil. Mag., 1916; also Bulletin No. 15 of the Indian Association) that at a particular pitch known as the wolf note pitch, a very peculiar beating note can be produced which however can be controlled by sufficiently large bowing pressure. He also showed that similar beating notes can be obtained at half the wolf note pitch. I have found that this sort of beating note can be obtained *e.g.*, in a violin at a large number of pitches, some of which are as strong as that at the wolf note pitch. They can, however, be controlled by increasing the bowing pressure. A little practice in bowing is necessary as some of them are produced by pressure varying within a small range.

[2] Bulletin No. 15, Indian Association for the Cultivation of Science.

# A STUDY OF THE EFFECT OF ADSORBED GAS ON THE HIGH-FREQUENCY RESISTANCE OF COPPER WIRE.

BY AUSTIN BAILEY.

SYNOPSIS.

*Effect of Adsorbed Gas on the High-frequency Resistance of a Loop of Copper Wire.*—This resistance is known to be greater than would theoretically be expected if the surface layers have the same resistivity as the core. The experiments described were undertaken to determine whether this increased resistance is due to gas adsorbed by the surface layer of oxide. A square loop, 60 cm. on a side, was formed by enclosing copper wires inside of glass tubes connected to a vacuum pump, and after several hours' preliminary heating and pumping, the wire was glowed, and then its resistance for radio-waves of 20 meters length was found to increase in 20 minutes by several per cent., though the residual pressure was only $10^{-5}$ atm. After successive glowings the effect became progressively less as the oxide layer disappeared. With higher pressures the increase to an equilibrium value came more rapidly. These results indicate that the gas adsorbed by the copper-oxide layer does increase the resistance, and suggest that possibly copper wire whose surface is covered with a thin layer of metal such as tin, might have a lower high-frequency resistance than oxidized copper wire of the same size.

*Short radio-waves, of less than 20 meters* were produced by using only the capacity of the oscillating triode tube in the high-frequency circuit. The wave-length was measured to within ½ per cent. by use of a modified Lecher System, with a hot-wire galvanometer at a current loop. Currents in the square loop were measured by means of a loosely coupled circuit containing a special vacuum thermo-element with minimum coupling in the galvanometer circuit.

*Adsorption of Gases by Copper Oxide and Copper.*—The observations indicate that copper oxide readily absorbs gases at room temperature and liberates them when glowed, while copper does not.

*An arc-type diffusion pump* is described, which has an iron wire ballast resistance wound around the tube which conducts the vapor to the condensation chamber. This enables the pump to get into operation quickly.

## INTRODUCTION.

AT very short wave-lengths, measurements made of the high frequency resistance of a one meter square loop of wire show a much larger value than that calculated from the formula for the resistance of a straight wire of the same length. The comparison between the observed and calculated values of the resistance of a one meter square loop of No. 18 B. & S. gauge copper wire are shown in Fig. 1.

This discrepancy may be due to a number of causes, one of which may be gas adsorbed on the surface of the wire. Langmuir[1] has pointed out that there is probably a very close packing of the gas molecules adsorbed

[1] I. Langmuir, PHYS. REV., *8*, 149 (1916).

on the surface of a metal. Such a condensation would doubtless alter materially the physical properties of the surface. Since at high frequency, a large part of the current will flow in a thin skin near the surface, a change in the high-frequency resistance would be expected if we changed the properties of that surface.

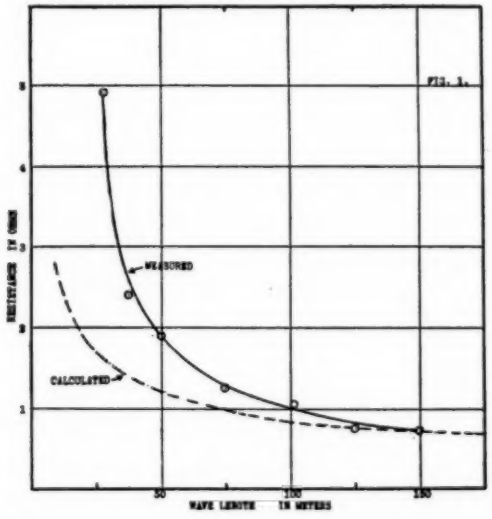



Fig. 1.

The experiments described below were undertaken in order to determine whether such a change of resistance due to a gas skin could be detected. The effect, if it exists, would be especially marked in some material which is known to adsorb gases strongly. Now Merton[1] has found that "copper strongly absorbs most gases." I, therefore, formed a square loop of copper wire, enclosing it in a glass tube so that the condition of the wire surface could be altered at will and measured the current flowing in the wire. A change in the resistance in the circuit, if capable of detection under the limitations of these experiments would then be indicated by a change in the reading of the galvanometer, since the electromotive force induced in the circuit was maintained constant.

## TEST CIRCUIT.

The copper wire 0.045 cm. in diameter and about 240 cm. long was mounted at the center of a glass tube. The tube was made in two L sections which were so placed together as to form a square 64 cm. on each side, and were interconnected to the vacuum system as shown in Fig. 2. At the corner of each L tube the wire was supported by a Pyrex

[1] T. R. Merton, Chem. Soc. Jour., *105*, 645 (1914).

glass insulator *I*, connected at its far end to a spring *S*, which extended out into a small side arm which made equal angles with the sides of the L. By this means the wire was kept taut.

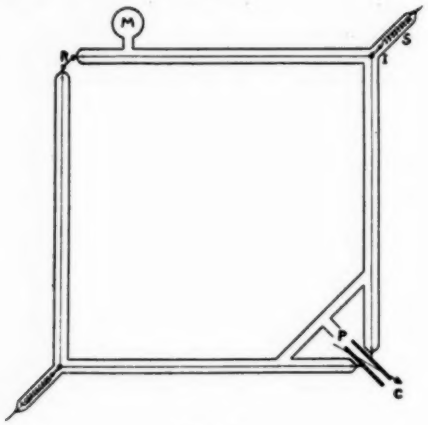



Fig. 2.

At the ends of each L the wire was attached to a piece of 1.05 mm. platinum wire and sealed out through the end, so that two of the corners of this square could be used for connecting additional apparatus. At one of these corners a single plate variable air condenser *C* was connected, and at the other corner an arrangement was made for connecting in various standard high frequency resistances, *R*, by means of mercury cups. Thus the resistance of the circuit could be measured by adding into the circuit known resistances.

## MEASURING CIRCUIT.

To determine the change in current in the test circuit produced by different conditions of the wire, a circuit containing a 20 cm. loop of

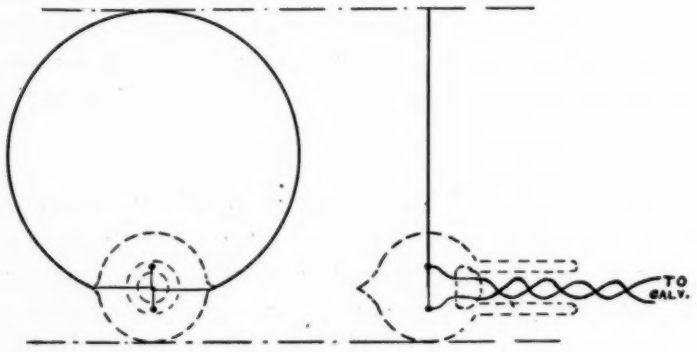



Fig. 3.

wire closed at its end by a thermo-element was inductively coupled to this circuit. The thermo-couple was especially designed and constructed so as to have as small currents as possible induced in the galvanometer circuit. This was done by making the plane of the loop at right angles to the galvanometer connections and by twisting together the insulated leads to the galvanometer as shown in Fig. 3. The copper-constantan element itself was mounted in a bulb which was evacuated to reduce thermal losses.[1] This increases the sensitiveness of the couple.[2] The measuring circuit being very sensitive could be loosely coupled to the test circuit and thus introduce only a very small resistance into the latter. At the same time it could be so placed that its loop plane was perpendicular to that of the oscillator circuit and thus reduce to a minimum direct action from the source of the power.

## OSCILLATOR.

A three-electrode vacuum tube connected as shown in the diagram (Fig. 4) was used as a high-frequency generator.

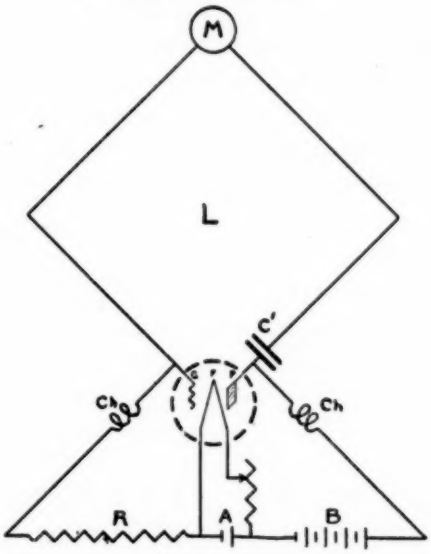



Fig. 4.

From the diagram it can be seen that the oscillating circuit contains only the capacity of the tube, in series with a blocking condenser $C'$, of $\frac{1}{2}$ $\mu$f. and the inductance of a loop of wire 100 cm. square, $L$. The hot-wire ammeter $M$ is placed at a current loop so that it will indicate that the circuit is oscillating. The chokes $Ch$ were so adjusted that they

[1] I. Klemencic, Wied. Ann., *42*, 416 (1891).

[2] P. Lebedew, Ann. d. Phys., 4 s., *9*, 209 (1902).

were resonant at a frequency slightly greater than the frequency generated by the oscillating circuit. Such an adjustment makes the chokes have a high inductive reactance at the frequency used, and prevents the high-frequency current from going back into the direct-current circuits. A negative potential of about 100 volts is maintained on the grid by means of the grid-leak resistance $R$. Any desired potential on the plate could be obtained by means of a potentiometer contact on a resistance, through which the current from a 300-volt generator was maintained constant by means of a ballast lamp. This circuit, with the exception of the power supply, was mounted on a movable base, so that the angle of the loop with reference to the test circuit could be altered by rotation about two axes. The coupling could also be changed by altering the position of the oscillator with reference to the test circuit.

## MEASUREMENT OF FREQUENCY.

A wave-meter was made of a variable air condenser with a maximum capacity of 670 $\mu\mu$f. and a single loop of No. 10 B. & S. gauge copper wire 20 cm. in diameter. The resonance point was indicated by a hot-wire galvanometer inductively coupled to this. By courtesy of the Commanding Officer, Radio Laboratories, Camp Alfred Vail, New Jersey, use was made of the Lecher system of parallel wires, constructed there by the author during the war, for the purpose of calibrating the wave meter. In Fig. 5 is shown the arrangement of the circuit. The single-

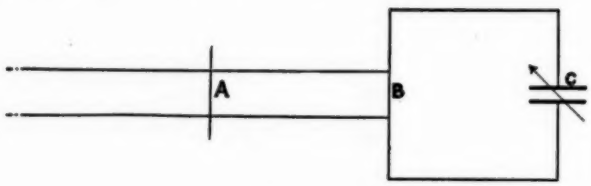



Fig. 5.

plate variable air condenser $C$ was adjusted so that resonance with an outside source was obtained in the loop circuit. The resonance point was very sharp, due to the low resistance of the circuit, and was indicated by placing the hot-wire galvanometer at the point $B$. By this method the parallel wires were directly coupled to a circuit of fixed frequency and standing waves were produced on them. The wires were very long in comparison with the wave-lengths to be measured.

To measure the wave-length, a wire-bridge mounted on a long insulating handle was slid along the parallel wires until the hot-wire galvanometer at $B$ showed a sudden decrease in reading to about half of its former

value. Suppose this position was $A$, then the distance $AB$ is some number of half wave-lengths. If the position $A$ is the first such position found after leaving $B$, then $AB$ is one half wave-length. A large number of current loops could be located in this manner, but since each position was more accurate than required, only two such determinations were made. While the method employed to determine the wave-length is similar to that described by Rubens,[1] the use of a small hot-wire galvanometer immediately at a current loop to indicate the positions of other current loops is believed to be of considerable advantage.

With an oscillating vacuum tube used to excite the system, the positions of $A$ could easily be located so that the value of the wave-length thus determined was accurate within 0.5 per cent. The accuracy of this method for giving the correct indication of wave-length was checked down to 38 meters wave-length by a wave-meter composed of a standard inductance,[2] and a variable air condenser, both calibrated by the Bureau of Standards.

## Vacuum System.

An oil pump which was capable of reducing the pressure to about 1 mm. of Hg was connected through a three-way stopcock to a drying tube containing $P_2O_5$. To the other end of the drying tube there was connected a system of two mercury condensation pumps in series. These pumps were made of Pyrex glass and connected by means of graded glass seal [3] to the McLeod gauge[4] and mercury trap. The design of the pumps is shown in Fig. 6. An arc[5] was used as the source of the vapor which was then conducted to the condensation chamber through a half-inch tube wound its entire length with No. 18 B. & S. gauge soft iron wire, with a cord, soaked in water-glass, wound between turns for insulation. To reduce the heat loss a covering of woven asbestos tape was wound on outside of the wire layer. The iron wire keeps the tube conducting the vapor warm[6] and at the same time acts as a ballast resistance for the arc. Tests made with this pump showed that its maximum rate of pumping was obtained when it consumed 300 watts and that the way in which this power was applied made no difference, *i.e.*, it could all be put into the arc, using external resistance, or it could be put into the arc and the resistance wound around the tube conducting

[1] H. Rubens, Wied. Ann., *42*, 154 (1891).
[2] Circular 74 of the Bureau of Standards, page 320.
[3] W. C. Taylor and Austin Bailey, Jour. Ind. Eng. Chem., *13*, 1158 (1921).
[4] Austin Bailey, Phys. Rev., *15*, 319 (1920).
[5] L. T. Jones and H. O. Russell, Phys. Rev., *10*, 301 (1917).
[6] Gaede, Ann. Phys., *4*, 46, 357 (1915).

the mercury vapor to the condensation chamber. The latter method of applying the power was, however, found to have the distinct advantage of making the pump effective sooner after closing the switch and at the same time of requiring a smaller current for operation.

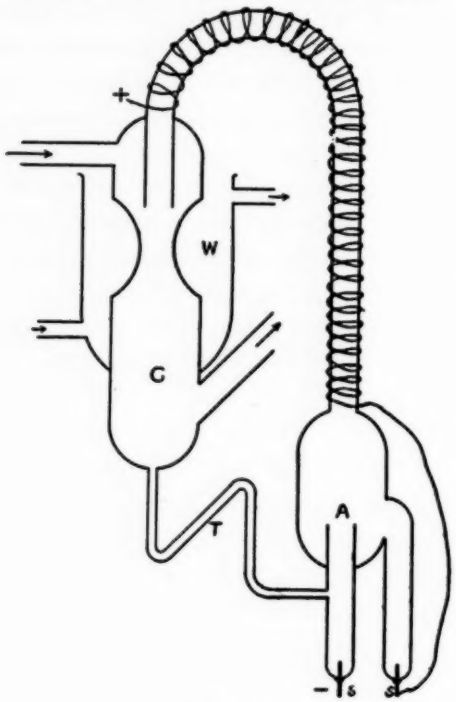



Fig. 6.

## OBSERVATIONS AND CONCLUSIONS.

With the apparatus arranged as described above, I first removed from the surface of the wire and the walls of the containing glass tube much of the adsorbed gas. This was accomplished by placing around the tube containing the wire an electrical resistance furnace and heating the glass to about 250° C., while at the same time the wire was raised to a much higher temperature by passing a current of about 2 amperes through it. This boiling-out process was continued for from three to four hours and then the tube containing the wire was sealed off from the pumping system. I then removed the furnace from the wire and allowed the apparatus to cool to the temperature of the room.

At the end of this process the surface of the wire was apparently covered with a layer of oxide. To remove any adsorbed gas from this surface layer, the wire was heated as hot as possible without burning out, and the observations begun immediately afterwards. The observa-

tions were continued until there appeared to be no further change in the resistance of the wire. Expansion of the wire caused by the increase in temperature, temporarily changed the inductance of the circuit. To compensate for this change, the circuit was constantly retuned during the cooling of the wire by adjusting the variable condenser $C$ shown in Fig. 2. This adjustment was made at a distance from the circuit by means of a cord wound around the condenser handle, which enabled the observer to tune accurately without influencing the circuit by the close proximity of his body. The position of the observers remained fixed during each set of observations.

The attached curves show the results of several such runs. Fig. 7 shows successive runs on a wire which had previously been boiled out as described above. Two heatings of the wire to red heat were made to drive off adsorbed gas. This raised the pressure in the tube to about $4 \times 10^{-3}$ mm. of Hg as indicated by the appearance of the discharge through the tube from a spark coil. One day later the wire was again heated red hot and beginning twenty minutes later the series of observations shown in Fig. 7 were made. The initial decrease in the resistance

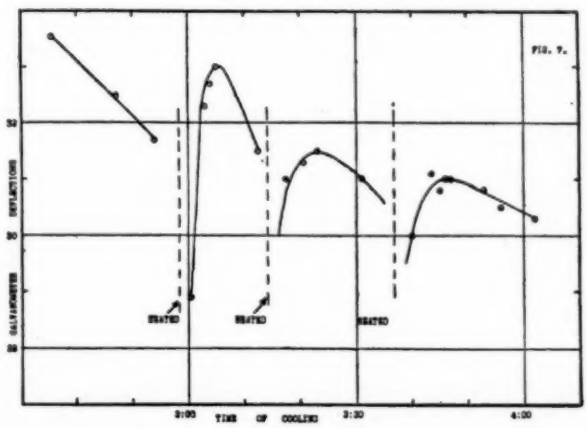



Fig. 7.

of the wire, shown by the rising portion of the curves, is obviously due to the cooling of the wire, for the tests made of the time required to obtain a maximum reading with the temperature of the test circuit constant proved that this gradual increase could not be due to the sluggishness of the measuring circuit. The subsequent decrease of reading is attributed to the readsorption of a film of gas by the oxide surface. As this takes place slowly at low pressures the galvanometer deflections go through a maximum, showing that the wire has a decreased resistance for a few

minutes after the wire has cooled and before the gas has had time to be completely readsorbed. The progressive decrease in the ordinates of successive curves in the series shown in Fig. 7 is probably due to the discharge of the storage battery of 40 amp.-hours' capacity which was running the motor-generator and discharging at an 8 amp. rate. The increase in the brightness of the appearance of the wire after successive heatings indicated that the flattening out of the maximum was probably due to the removal of the oxide covering, thus decreasing the asdorbing surface.

The same wire used in Fig. 7 was heated in the resistance furnace again for four hours at about 250° C. and the appearance of the wire surface changed from a bright copper color to a reddish brown, showing that the oxide layer which had been decomposed by the heatings previously given to it had been partially reformed. The behavior of this wire, plotted in Fig. 8, was similar to that shown in Fig. 7. No quantita-

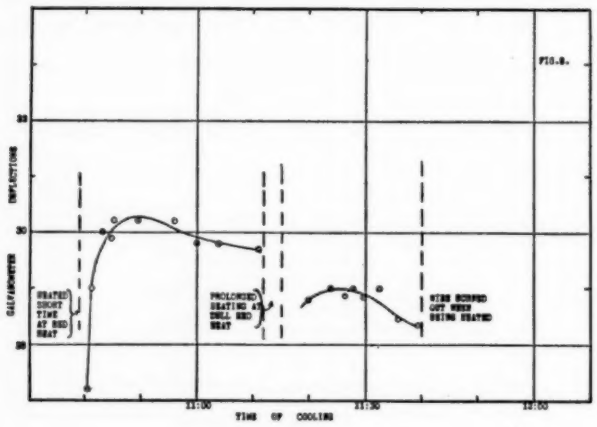


Fig. 8.

tive comparison can be made between these two figures or those following because of changes made in the position of the measuring circuit. Unfortunately the wire burned out during the third heating and a complete series could not be obtained.

The curves plotted in Figs. 9 and 10 are made with a different wire. Previous to the first curve plotted in Fig. 9 the wire had been boiled out and sealed off in a tube, and had been allowed to stand several days. The pressure in this tube was not as low as in the tube previously used. An interval of $7\frac{1}{2}$ hours elapsed before the first curve in Fig 9, during which time the storage battery was recharged. The curve following this charge of the storage battery is very erratic and full of accidental variations but it shows strong indication of a maximum. The next curve

is more consistent in its points and fewer abrupt changes in galvanometer deflections were observed.

On allowing the air to again fill the tube at atmospheric pressure no marked change occurred. (See Fig. 9.) After heating the wire in air

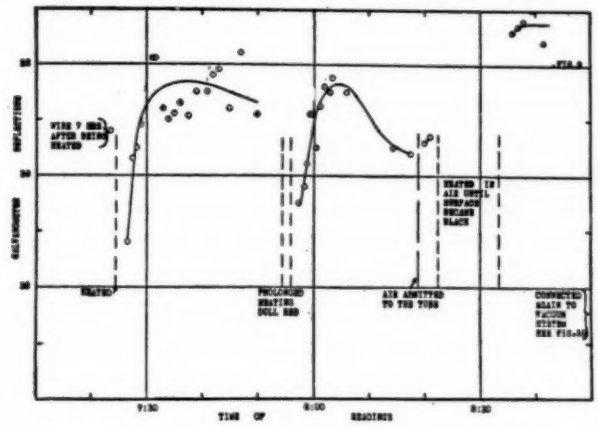


Fig. 9.

for ten minutes its surface appeared almost black, due undoubtedly to the formation of cupric oxide, CuO. Immediately after the heating current was turned off the oscillator was started again and observations made of the galvanometer deflections. These show a slight indication of a maximum. If this is a true maximum it is probably due to the same cause as before but is much sharper because the wire was initially at a lower temperature, could cool more quickly, and would probably readsorb gas more rapidly at atmospheric pressure.

The oscillator was again stopped, the tube connected to the vacuum

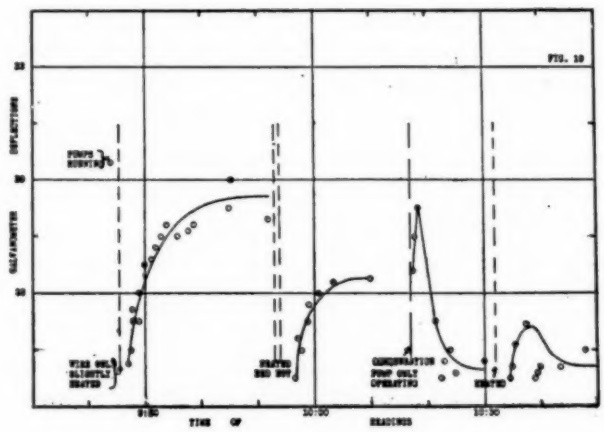


Fig. 10.

system and the pressure reduced to $3 \times 10^{-4}$ mm. of Hg. The next two curves (Fig. 10) taken while the pumps were running, shows no maximum, probably because at this low pressure the gas was readsorbed more slowly by the oxide layer after heating. After the second heating at this low pressure the wire was apparently covered with the red oxide, $Cu_2O$. When the mercury condensation pumps were turned off and the backing pump still kept operating, the pressure gradually increased. The mercury in the pumps was so hot that it continued to go over and condense for some time after the current was turned off. This continued operation of the mercury pumps thus allowed the pressure to increase gradually. The first abrupt rise of the third curve shown in Fig. 10 may be due to some cause connected with stopping the operation of the mercury pumps, since the circuit at this frequency is very subject to variations from slight changes in nearby circuits. The final decrease of the galvanometer deflection however is probably due to the readsorption of the gas as the pressure increased.

Any single curve taken by itself would probably have little or no significance owing to the large fluctuations in the readings, due to accidental influences, but all the curves taken together strongly indicate: (1) that gas is readily adsorbed by copper oxide, and is easily liberated by heating, (2) that copper either does not adsorb gases as readily or that the adsorbed layer is not as easily liberated from the copper by heating, (3) that the resistance of the wire to high frequency currents is increased by the presence of the gas skin.

The "precipitated copper" as used by Merton was doubtless largely cuprous oxide as he describes it as "very dark brown in color," and as "prepared by reducing a solution of the copper salt." As is well known $Cu_2O$ is prepared in this way. Finely divided copper can also be prepared in this way by the addition of suitable reducing agents such as $N_2H_4H_2O$. His statement that "if the copper is too strongly heated, it undergoes a change in color and loses its absorbing power," would also tend to show that the "precipitated copper" was largely $Cu_2O$ and that on heating too strongly it underwent a chemical change, probably becoming metallic copper. Thus interpreted, his results are in entire agreement with the conclusions given above.

Copper wire when used commercially is doubtless covered with a thin layer of oxide, which strongly adsorbs gases, and which therefore according to the above results increases the resistance of the wire. Covering the surface of the wire with some metal which does not easily oxidize and at the same time does not appreciably adsorb gases would probably decrease the resistance of the wire. Possibly tin-covered

copper wire would prove to have a lower high-frequency resistance than copper wire of the same size.

In closing, I wish to express my keen appreciation of the interest shown and encouragement given in this work by Professor Ernest Merritt and of the coöperation of Professor R. C. Gibbs in obtaining the material necessary to work out this problem. The advice and suggestions given by other members of the Department of Physics throughout the progress of this research is also greatly appreciated. Likewise, I wish to acknowledge the generous assistance which I have received from Professor Ernest Merritt and Doctor Gordon S. Fulcher in preparing this material for publication.

Cornell University,
June, 1920.

# ELECTROMAGNETIC WAVES IN ABSORBING MEDIA.

BY LEIGH PAGE.

SYNOPSIS.

*Specific Intensities of Radiation in Two Media in Thermal Equilibrium.*—If the media are transparent, the specific intensity of radiation $K$ is proportional to the square of the index of refraction, as was shown by Kirchhoff. In dealing with absorbing media Planck assumes that $K$ is proportional to the square of the real part of the complex index. Laue has questioned the validity of this assumption and has published an investigation of the problem purporting to show that $K$ is proportional to the square of the modulus of the index of refraction. Laue, however, has treated incident and reflected waves in an absorbing medium as separate entities in computing energy fluxes, a method which is not legitimate when a change in phase occurs at reflection. The *mathematical investigation of the problem* given in this paper confirms Planck's assumed proportionality in the case of moderately absorbing media. In intensely absorbing media it is doubtful if it is legitimate to substitute trains of plane waves of equal intensity moving in all directions for the irregular fluxes due to emission and absorption in the medium.

*Energy Flux for Homogeneous Plane Waves Incident on the Plane Surface of an Absorbing Medium.*—Equations are derived for the energy reflected and the energy transmitted. On account of the difference in phase between incident and reflected waves the rate of absorption near the surface varies with the phase; in fact, it is negative for part of each period.

IN the theory of heat radiation it is of interest to investigate the relation between the specific intensities of radiation $K$ of a given frequency in two media in thermal equilibrium with each other. The relation for the case of transparent media, given by Kirchhoff,[1] is obtained very easily. Let subscripts $_1$ and $_2$ refer to the two media and suppose the surface of separation to be smooth and plane. Then the energy of plane polarized waves incident at angle $\phi_1$ (Fig. 1) in the first medium inside the conical angle $d\Omega_1$, per unit area of the surface of separation, per unit time, per unit frequency range, is

$$K_1 \cos \phi_1 \, d\Omega_1.$$

If $r_1$ is the coefficient of reflection, the energy reflected is

$$r_1^2 K_1 \cos \phi_1 \, d\Omega_1.$$

Hence the energy transmitted into the second medium is

$$(1 - r_1^2) K_1 \cos \phi_1 d\Omega_1 = (1 - r_1^2) K_1 \cos \phi_1 \sin \phi_1 d\phi_1 d\gamma, \qquad (1)$$

$\gamma$ being the azimuth.

[1] G. Kirchhoff, Gesammelte Abhandlungen, p. 594, 1882.

Equating to this a similar expression for the energy transmitted from the second into the first medium, and making use of Snell's law

$$\nu_1 \sin \phi_1 = \nu_2 \sin \phi_2,$$

where $\nu$ is the real index of refraction, it follows that

$$\frac{K_1 \nu_2^2}{K_2 \nu_1^2} = \frac{1 - r_2^2}{1 - r_1^2}. \tag{2}$$

But, the electromagnetic theory of light gives

$$r_1^2 = r_2^2.$$

Hence

$$\frac{K_1}{K_2} = \frac{\nu_1^2}{\nu_2^2}. \tag{3}$$

In his book on heat radiation,[1] Planck states this law in the form "the specific intensities of radiation of a certain frequency in the two media are in the inverse ratio of the squares of the velocities of propagation, or in the direct ratio of the squares of the indices of refraction," and, while his proof is limited to transparent media, he assumes that the result holds for absorbing media.

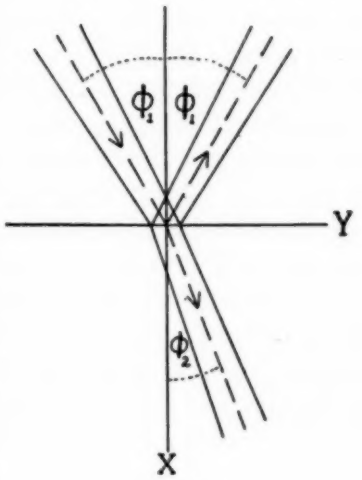


Fig. 1.

Laue[2] has questioned the validity of extending this relation to the case of absorbing media, and concludes that in this case the ratio should be that of the squares of the *moduli* of the complex indices of refraction, instead of the squares of the *real parts* of these indices, as Planck implies. The difficulty in using Planck's method of derivation in the case of absorbing media lies in the fact that except in special cases a homogeneous plane wave incident in one medium will be transmitted into the other as an unhomogeneous plane wave. In the latter type of wave the flux of energy is not continuously along the wave normal, but varies in direction as the phase changes. Hence the energy in the refracted wave is scattered, and Snell's law cannot be applied.

Laue's method of attacking the problem is this. He considers first equilibrium between two media whose indices of refraction have the

[1] The Theory of Heat Radiation (Masius), p. 35, 1914.

[2] Ann. d. Phys., 32, 1085, 1910.

same arguments but different moduli for waves of the particular frequency under consideration. In this case a homogeneous plane wave in one medium will remain homogeneous on passing into the other, and hence the method of derivation used by Planck for transparent media applies. For if the complex absolute index of refraction is denoted by.

$$N = ne^{i\psi} = \nu(1 + ix),$$

then the relative index

$$\frac{N_1}{N_2} = \frac{n_1}{n_2},$$

will be real for equal $\psi$'s in the two media. Hence in place of (3) is obtained the relation

$$\frac{K_1}{K_2} = \frac{n_1^2}{n_2^2}. \tag{4}$$

In order to find out how this relation involves the argument of the index, Laue next considers two media (one may be vacuum) whose indices of refraction have the same moduli but different arguments. He assumes that the irregular radiation passing through any point of the medium is equivalent to trains of homogeneous plane waves of equal intensity traveling in all directions, insofar as the average flux of energy is concerned. Then he takes expression (1) for the energy transmitted through the surface, where $r$ is the modulus of the now complex coefficient of reflection. Integrating over a hemisphere he gets an expression for the energy transmitted from the first medium into the second. By the same procedure a corresponding expression is obtained for the energy flowing through the surface from the second medium into the first. In the state of equilibrium these expressions must be equal. But the integrands are the same, and as there is no total reflection the limits of the two integrals are the same. Hence

$$\frac{K_1}{K_2} = 1, \tag{5}$$

and Laue concludes that the ratio of the specific intensities is not a function of the arguments of the indices of refraction of the media. Hence, in general, this ratio must equal the ratio of the squares of the moduli, whereas Planck has assumed it equal to the ratio ot the squares of the real parts of the indices of refraction.

Laue's method is open to objection on the score that it is not obviously legitimate to replace the irregular radiation produced by absorption and reëmission in a medium which is not transparent by trains of homogeneous plane waves of equal intensity moving in all directions. This

ideal condition, which must be assumed in order that the mathematical analysis of the problem may not become hopelessly involved, would seem to be less permissible the more strongly absorbing the medium, and the shorter the distance waves can proceed from their sources without being greatly reduced in intensity.

However, a closer examination of the problem does not confirm Laue's conclusion that the ratio of the specific intensities of radiation is independent of the arguments of the indices of refraction even when his method of analysis is followed. For Laue has assumed that incident and reflected waves in an absorbing medium may be treated as separate entities in computing the energy transmitted across the surface. This assumption would be legitimate if there were no change in phase on reflection. The change in phase, however, results in a transmission through the surface of an amount of energy greater than the difference between that brought up in the incident wave and that taken away in the reflected wave. This is in no way contradictory to the principle of conservation of energy, as the energy absorbed near the surface supplies the excess of energy transmitted over that accounted for by the difference of incident and reflected energies.

The object of this paper is to investigate by Laue's method the ratio of the specific intensities in two media which have the same moduli but different arguments in their indices of refraction. Without loss of generality one of the media may be assumed to be vacuum. The modulus of the index of refraction of the other, then, will be unity. It is shown below that for *moderately* absorbing media, Laue's equation (5) should be

$$\frac{K_1}{K} = \cos^2 \psi_1, \tag{6}$$

where $K$ refers to vacuum. Hence combining with (4), it is seen that in the general case where both moduli and arguments differ in the two media,

$$\frac{K_1}{K_2} = \frac{n_1^2 \cos^2 \psi_1^2}{n_2^2 \cos^2 \psi_2} = \frac{v_1^2}{v_2^2}, \tag{7}$$

which is the relation deduced by Kirchhoff and Planck for transparent media. Hence Planck's extension of this relation to absorbing media is justified, at least for the case of *moderate* absorption. In the case of intensely absorbing media, it is doubtful if the substitution of trains of homogeneous plane waves for the energy fluxes actually present is legitimate.

Consider a homogeneous plane wave proceeding through an absorbing

medium in the direction of the $X$-axis. Let the electric vector $E$ and displacement $D$ have the direction of the $Y$-axis. Then the magnetic vector $H$ will lie along the $Z$-axis. If $\omega/2\pi$ is the frequency of the radiation, and $S$ stands for the wave slowness *in vacuo*, the electromagnetic equations give

$$E = Ae^{-\omega n \sin \psi S x} e^{i\omega(n \cos \psi S x - t)},$$
$$H = Ane^{-\omega n \sin \psi S x} e^{i[\omega(n \cos \psi S x - t) + \psi]},$$
$$D = An^2 e^{-\omega n \sin \psi S x} e^{i[\omega(n \cos \psi S x - t) + 2\psi]}.$$

The Poynting flux is continuously in the $X$ direction and amounts to

$$s = cEH$$
$$= \tfrac{1}{2}cA^2 ne^{-2\omega n \sin \psi S x}\{\cos \psi + \cos [2\omega(n \cos \psi S x - t) + \psi]\}, \quad (8)$$

and the energy density

$$u = \int E\dot{D}dt + \tfrac{1}{2}H^2$$
$$= \tfrac{1}{2}A^2 n^2 e^{-2\omega n \sin \psi S x}[\cos \psi\{\cos \psi + \cos [2\omega(n \cos \psi S x - t) + \psi]\}$$
$$+ \sin \psi\{2\omega t \cos \psi - \sin [2\omega(n \cos \psi S x - t) + \psi]\}. \quad (9)$$

But the energy propagated in the form of waves must be equal to the Poynting flux divided by the velocity of propagation $q$, that is,

$$u_1 = \frac{s}{q}$$
$$= \frac{n \cos \psi}{c} s$$
$$= \tfrac{1}{2}A^2 n^2 e^{-2\omega n \sin \psi S x} \cos \psi\{\cos \psi + \cos [2\omega(n \cos \psi S x - t) + \psi]\}, \quad (10)$$

and, as the coefficient of absorption is evidently

$$\alpha = 2\omega n \sin \psi S,$$

the energy absorbed is

$$u_2 = \int \alpha u_1 q dt$$
$$= \tfrac{1}{2}A^2 n^2 e^{-2\omega n \sin \psi S x} \sin \psi\{2\omega t \cos \psi - \sin [2\omega(n \cos \psi S x - t) + \psi]\}. \quad (11)$$

The sum of $u_1$ and $u_2$ checks with $u$, as it should.

Now it appears from (11) that the rate of absorption is not the same at different points along the wave, but varies with the phase. Fig. 2 is a graph of $E$, $H$, $D$, $u_1$ and $s$. The curve giving the rate of absorption of energy has the same form as that for the energy $u_1$ propagated by the wave. It will be noted that this curve lies below the horizontal axis wherever $E$ and $H$ have opposite signs. In these regions the rate of absorption is negative, that is, the medium is returning to the wave energy previously absorbed.

Consider now a train of homogeneous plane waves incident in the

absorbing medium 1 (Fig. 1) at the angle $\phi_1$. This medium has an index of refraction with unit modulus, *i.e.*, $n$ is unity. Medium 2 is vacuum, and quantities referring to it will be denoted by letters without subscripts.

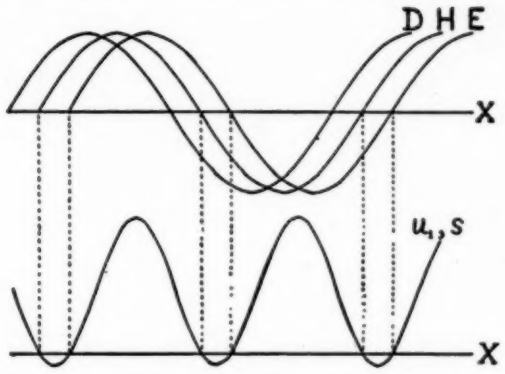



Fig. 2.

Confining attention to plane polarized waves with the electric vector normal to the plane of incidence, at the surface

$$E_{1_z} = A_1 e^{i\omega(\cos\psi_1 S_y \sin\phi_1 - t)},$$
$$H_{1_z} = A_1 \sin\phi_1 e^{i[\omega(\cos\psi_1 S_y \sin\phi_1 - t)+\psi_1]},$$
$$H_{1_y} = -A_1 \cos\phi_1 e^{i[\omega(\cos\psi_1 S_y \sin\phi_1 - t)+\psi_1]},$$

in the incident wave. The complex coefficient of reflection may be written

$$R_{1_\perp} = r_{1_\perp} e^{i\theta_{1_\perp}}.$$

Then in the reflected wave

$$E_{1_z}' = r_{1_\perp} A_1 e^{i[\omega(\cos\psi_1 S_y \sin\phi_1 - t)+\theta_{1_\perp}]},$$
$$H_{1_z}' = r_{1_\perp} A_1 \sin\phi_1 e^{i[\omega(\cos\psi_1 S_y \sin\phi_1 - t)+\psi_1+\theta_{1_\perp}]},$$
$$H_{1_y}' = r_{1_\perp} A_1 \cos\phi_1 e^{i[\omega(\cos\psi_1 S_y \sin\phi_1 - t)+\psi_1+\theta_{1_\perp}]}.$$

Now, the flux of energy through the surface is

$$s_{1_z} = -c[E_{1_z} H_{1_y} + E_{1_z}' H_{1_y}' + E_{1_z} H_{1_y}' + E_{1_z}' H_{1_y}].$$

If there were no change in phase on reflection the last two terms in the brackets would be equal and opposite in sign. Laue's result is due to his omission of these terms.

Substituting the values of the electric and magnetic intensities, and averaging over a period,

$$\bar{s}_{1_z} = \tfrac{1}{2} c A_1^2 \cos\phi_1 \cos\psi_1 [(1 - r_{1_\perp}^2) + 2 r_{1_\perp} \sin\theta_{1_\perp} \tan\psi_1]. \qquad (12)$$

The first term represents the difference between the energy brought

up by the incident waves and that carried away by the reflected waves; the last term represents energy which had previously been absorbed by the medium close to the surface and is now transmitted across the surface into the vacuum in the form of waves. In fact, an investigation of absorption near the surface shows that the phase relation between reflected and incident waves is such that more than the average absorption occurs in this region. This excess absorption just accounts for the excess energy transmitted across the surface.

For waves with the electric vector in the plane of incidence, the same method of investigation gives [1]

$$\bar{s}_{1_x} = \tfrac{1}{2}cA_1^2 \cos\phi_1 \cos\psi_1[(1 - r_{1_{||}}^2) - 2r_{1_{||}} \sin\theta_{1_{||}} \tan\psi_1]. \quad (13)$$

Now

$$\tfrac{1}{2}cA_1^2 \cos\psi_1 = K_1 \sin\phi_1 d\phi_1 d\gamma.$$

Therefore, taking both states of polarization into account, and integrating over a hemisphere, the total energy passing from the medium into the vacuum is

$$\bar{s}_{1_x} = 2\pi K_1 \int_0^{\pi/2} \cos\phi_1 \sin\phi_1 d\phi_1[(2^2 - r_{1_\perp}^2 - r_{1_{||}}^2) + 2\tan\psi_1 (r_{1_\perp} \sin\theta_{1_\perp} - r_{1_{||}} \sin\theta_{1_{||}})].$$

Calculating the coefficients of reflection and substituting their values in this expression

$$s_{1_x} = 8\pi K_1 \sec\psi_1 \int_0^{\pi/2} c\cos^2\phi_1 \sin\phi_1 d\phi_1 \left\{ \frac{\cos d}{\cos^2\phi_1 + c^2 + 2c\cos\phi_1 \cos(\psi_1 - d)} + \frac{\cos d}{\cos^2\phi_1 + c^2 + 2c\cos\phi_1 \cos(\psi_1 + d)} \right\}, \quad (14)$$

where

$$ce^{id}$$

is the complex cosine of refraction.

Following the same procedure in calculating the energy passing from the vacuum into the medium, the final terms in the expressions corresponding to (12) and (13) are absent as $\psi$ is zero. In this case the total flux is

$$\bar{s}_x = 8\pi K \int_0^{\pi/2} c_1 \cos^2\phi \sin\phi d\phi \left\{ \frac{\cos(\psi_1 + d_1)}{\cos^2\phi + c_1^2 + 2c_1\cos\phi\cos(\psi_1 + d_1)} + \frac{\cos(\psi_1 - d_1)}{\cos^2\phi + c_1^2 + 2c_1\cos\phi\cos(\psi_1 - d_1)} \right\}$$

[1] As $r_{1_{||}} \sin\theta_{1_{||}}$ is negative, the last term in (13) is positive.

$$= 8\pi K \left[ \cos\psi_1 \int_0^{\pi/2} c_1 \cos^2\phi \sin\phi \, d\phi \left\{ \frac{\cos d_1}{\cos^2\phi + c_1^2 + 2c_1 \cos\phi \cos(\psi_1 + d_1)} + \frac{\cos d_1}{\cos^2\phi + c_1^2 + 2c_1 \cos\phi \cos(\psi_1 - d_1)} \right\} \right.$$

$$- 4 \sin^2\psi_1 \int_0^{\pi/2} \frac{c_1^2 \sin^2 d_1 \cos^3\phi \sin\phi \, d\phi}{[\cos^2\phi + c_1^2 + 2c_1 \cos\phi \cos(\psi_1 + d_1)][\cos^2\phi + c_1^2 + 2c_1 \cos\phi \cos(\psi_1 - d_1)]} \qquad (15)$$

Now, as $\sin d_1$ is of the order of $\sin\psi_1$, the last integral in (15) is of an order not less than $\sin^4\psi_1$ as compared with the first. Hence in the case of moderately absorbing media it can be neglected.

It can easily be shown that when $\phi_1$ equals $\phi$, $c = c_1$ and $d = -d_1$. Hence the integrand in (14) is identical with that of the first integral in (15) for equal values of $\phi_1$ and $\phi$. Equating these two expressions and canceling the equal integrals, equation (6) is obtained for moderately absorbing media.

The writer is indebted to Mr. N. I. Adams for calling his attention to the limitation of Planck's deduction of the relation between the specific intensities of radiation to the case of transparent media.

Sloane Physics Laboratory,
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# A TRANSITION OR ADSORPTION-LAYER THEORY OF THE E.M.F. OF THE VOLTAIC CELL.

BY R. D. KLEEMAN.

SYNOPSIS.

*Transition-Layer Theory of the Difference of Potential between an Electrolyte and a Metal Plate Immersed in It.*—Since the layer of solution adjacent to the plate is under the influence of the molecular forces of the metal plate on one side and under those of the liquid on the other, it will, in general, differ from the rest of the solution in density, in concentration of solute (adsorption), and in degree of dissociation; and because of the difference in the diffusion velocities of the positive and negative ions, a segregation of the ions will result which will produce an electric field through the layer and will also charge the plate and the solution oppositely. These two fields, one due to the asymmetrical distribution of ions (volume charge) and the other to the charge on the plate, together cause the potential difference observed between metal and solution. The theory explains the well-known phenomena of the voltaic cell and also leads to the *prediction of a number of new effects*. When equilibrium exists the rates of gain and of loss of charge, by diffusion of ions to the plate and by chemical action, must be equal. This equilibrium should take an appreciable time to establish initially, it should be affected by a magnetic field and should be different if there is relative motion between the plate and the liquid. Also, if this theory is correct, the e.m.f. of a voltaic cell should depend on the distance apart of the plates and should change when a direct or alternating current is sent through the cell; and two rods of the same metal but of different diameters should show a difference of potential when dipped in the same electrolyte. These effects will be looked for experimentally. The *general differential equations* for the difference of potential according to this theory are given, but contain various functions whose form is at present unknown.

*Transition layer at the free surface of a liquid* should show not only an adsorption effect but also a segregation of the charges which may be associated with the *electrical effects of bubbling through liquid.*

NUMEROUS theories have been proposed to explain the nature of the e.m.f. of a cell. The most successful one that has of late been proposed is that by Nernst. Briefly his theory may be stated as follows: When a metal is in contact with a liquid there exists a tendency of the metal to go into solution in an electrified condition, which would leave the metal plate oppositely charged. The magnitude of this tendency, which is measured by what Nernst calls the solution pressure of the ions, depends on the nature of the metal and the liquid or solution. Therefore, if two different metals are placed in the same liquid, or solution, a difference of potential may exist between them, which would give rise to the flow of an electric current on joining the plates by a wire. Qualitatively the theory explains well such cells as the Daniel, and cells

of a similar nature, but fails to do so in other cases without the introduction of additional hypotheses, especially in those cases where the metal does not appear to go appreciably into solution and the action of the cell is attended by the evolution of gases on the metal plates. Quantitative agreement of the formulæ deduced from the theory has been obtained only in special cases. It appears, therefore, that Nernst's theory of the e.m.f. of a cell requires modification, or that a new theory should take its place. It is evident or obvious on general chemical grounds that a metal in a liquid would tend to go into solution. But this might be a purely secondary effect as far as the production of an e.m.f. is concerned. In fact I will show that this is the case. A theory can be formulated which, as I will show in this paper, explains the production of an e.m.f. in all cases, by reference to well-known effects, and which indicates the existence of many interesting and important associated and subsidiary effects.

Let us consider a liquid or a solution in contact with a metal plate. Since the density of the metal is not likely to be the same as that of the liquid—in most cases it would be greater, the attraction exerted by an element of matter of the plate on an element of matter of the liquid at a given distance, would be different in magnitude from that obtained if both elements of matter belonged to the liquid. Accordingly the layer of liquid in the immediate vicinity of the plate would be subjected to a set of forces of different magnitude than a layer at some distance from the plate. The density of the liquid near the plate would therefore be different from that in the interior of the liquid, in fact, it would gradually change on passing from the immediate vicinity of the plate into the interior of the liquid. Since the attraction between two elements of matter decreases very rapidly with the increase of their distance of separation, the greater part of this change would take place in a very thin layer next to the plate which accordingly may be called the transition layer of the liquid. The thickness of the layer may be, however, it is of importance to point out, many times greater than the distance between two elements of matter at which the force they exert upon each other ceases to be of appreciable magnitude. It is evident that a modified layer of liquid will exist in the immediate vicinity of the plate whose thickness is at least equal to the radius of the sphere of action of a molecule of the plate. Another modified layer of liquid will exist adjacent to the first layer, since it is bounded on one side by a modified layer. The thickness of the second layer is equal to the radius of the sphere of action of a liquid molecule. A third modified layer will exist adjacent to the second layer, and so on. These layers will differ, the less from

each other, the greater the distance from the plate, and at a certain distance, which may be taken as the thickness of the total layer, the state of the liquid will not differ appreciably from that at a great distance from the plate.

The liquid in the transition layer will differ in other respects than density from the other parts of the liquid. Thus if the liquid is a solution the ratio of the mass of solute to solvent will vary from one plane in the layer to another, and differ on the whole from the ratio in the remaining part of the solution. This effect is well known and is called adsorption. In the case that the solute is an electrolyte other important effects may occur, which would give rise to an e.m.f. across the layer. According to the theory of dissociation, a number $\gamma$ of neutral molecules in the solution dissociate into ions each second. This number depends on the density of the solution, the concentration of the solute, and the temperature. It would, therefore, have different values in different parts of the transition layer. At the same time ions would become neutral molecules by recombination, the loss by recombination being equal to $\alpha n_1 n_2$, where $n_1$ and $n_2$ denote the concentrations of the positive and negative ions respectively, and $\alpha$ the coefficient of recombination. The value of $\alpha$ would also change from one part of the transition layer to another. If the rate of diffusion of the negative ions is different from that of the positive, as is usually the case, a partial separation of the ions of different signs will gradually take place. These rates of diffusion, it should be noted, will vary from one part of the layer to another, and will evidently depend on the direction of the diffusion with respect to the plate. In the immediate vicinity of the plate there is, therefore, likely to be a surplus of ions of one sign. The plate will accordingly become electrically charged through the motion of translation of the ions bringing them into contact with the plate, which effect is modified by the electrostatic attraction exerted by the plate on the ions. The sign of the electric charge on the plate very probably is the same as that of the ion which is in surplus near the plate. The plate will cease to charge up any further when the electrical gains and losses per second are equal. Corresponding to the charge on the plate an equal and opposite charge is distributed throughout the solution. This will give rise to an electrical field in the solution, which for convenience will be called the plate electrical field. The segregation of ions in the translation layer due to different migration velocities will give rise to another electric field which for convenience will be called the liquid transition layer field. Equilibrium exists when the migration of the ions under the action of the plate and transition layer electric fields, osmotic pressure,

etc., is such that there is, on the whole, no gain or loss of ions in any part of the layer and solution. It should be observed that the plate electric field by itself cannot exist. For in that case the ions in the solution corresponding to the electric charge on plate would gradually be drawn towards the plate, and the electric field thus disappear. If, however, a tendency exists for the ions to segregate in the solution so that ions of opposite sign to the charge on plate tend to move away from the plate, the existence of the plate electric field would become possible. This is a very important point in the theory.

Thus the effect of the segregation of ions would be to produce an electric field, extending in the main from the outer boundary of the transition layer to the plate. It might be represented by two layers of electricity of opposite sign separated by a dielectric whose inductivity varies from layer to layer, and whose thickness is equal to the thickness of the transition-layer.[1] The change in potential experienced on passing an electric charge from the remote side of the layer to the plate is the difference of potential between plate and solution and may be called the transition-layer difference of potential. The magnitude of this potential will depend on the nature of the metal, the nature and the concentration of the solution, and the temperature, since the density of the transition layer, and the relative distribution of solvent and solute, would depend on the molecular forces exerted by the metal plate on the solution. Therefore when two different metal plates are placed in the same solution an e.m.f. would exist between them which would be equal to the algebraical sum of the e.m.f.'s of the two transition layers. Therefore when two different metal plates are joined by a wire a current would flow from one to the other returning through the solution.

It should be carefully noted that the electric field between plate and solution, and the corresponding difference of potential, consists of two distinct parts, one due to the electric charge on the plate, and the other due to an asymmetrical distribution of ions in the solution. The plate electric field, we have seen, may be said to be the outcome of the transition-layer field. But no definite relation need exist between their magnitudes. Thus it might happen that the latter field is small in comparison with the former. We would then be dealing with a state of affairs to which Nernst's solution pressure theory may be applied. It appears, therefore, that the theory proposed gives the "mechanism" of Nernst's theory in the cases where it can be applied. But the proposed theory goes a good deal further, namely, in explaining the difference of po-

[1] Resembling the Helmholz's interfacial condenser, whose apparent formation the theory would explain.

tential in all cases, including the important case when the metal shows no tendency to go into solution.

It will be of interest to examine a case of this particular case more closely—say plates of platinum and carbon immersed in a solution of sulphuric acid. A transition layer will be formed at the surface of each plate, and the partial segregation of the + H, − OH, and − $SO_4$ ions, will give rise to a charging up of the plate without any metal necessarily going into solution, or any chemical change whatsoever taking place. The resultant differences of potential between the plates and the solution will not be the same since the transition layers will differ from each other on account of being bounded by different materials. On joining the plates by a wire a current will pass which will result in hydrogen being given off at one plate and oxygen at the other. Let us suppose that each plate gets completely covered by a layer of gas. If the gases were conductors of electricity like a metal the current would continue to flow but corresponding to a different difference of potential, since the liquid transition layers would now be bounded by plates of hydrogen and oxygen respectively. But on account of the non-conduction of the gases and the gradual obliteration of the liquid transition layers which are *in contact* with the plates, the current in practice will gradually decrease, and may stop altogether. This effect is known as polarization. It appears from the foregoing considerations that polarization in the various ways that it may occur can be strikingly explained by means of the proposed theory.

It will be of interest next to examine what happens according to the foregoing theory when a metal is immersed in a solution of an acid which dissolves the metal, say—a copper plate in a solution of $H_2SO_4$. The solutions will initially contain the ions + H, − OH, and − $SO_4$, which are partly segregated in the transition layer adjacent to the plate. The motion of translation of the ions will bring some of them in contact with the plate, giving rise to the formation of copper oxide and copper sulphate, the latter dissolving in the solution. These ions will give their electrical charges to the plate. The + H and − OH ions in coming in (proper) contact with the plate might give up their electrical charges without any chemical action taking place. The copper sulphate formed in the solution will give rise to the formation of + Cu and − $SO_4$ ions, and the electrical nature of the transition layer will undergo a corresponding change. This process will go on till equilibrium is reached, which corresponds to the number of copper atoms combining per second with − $SO_4$ ions being equal to the number of + Cu ions deposited on the plate. Now these numbers are evidently controlled by the electric

field of the liquid transition layer and that due to the charge on the plate. Thus the ultimate concentration of the copper sulphate solution would be determined by the transition layer adjacent to the plate.

It will be of interest to point out that the free surface of a solution should possess a similar transition layer with which an e.m.f. would be associated. In such a case the density of the layer will obviously decrease on passing from its lower side to the upper side or surface of the liquid. This would have the effect of producing an adsorption effect (which is well known), and a segregation of the electrical charges similar to what takes place when the solution is in contact with a metal plate. This layer is probably intimately associated with the electrical effects produced by the bubbling of gases through liquids.

The distribution of the electrical charges in a transition layer may be predicted in a general way from the foregoing considerations. Let us consider a metal plate of infinite area in contact with a layer of solution of infinite thickness. If the difference between the concentration of the positive and negative ions, or $n_1 - n_2$, is measured along a line at right angles to the plate, and plotted against the distance from plate which will be denoted by $x$, a curve of the general form shown in Fig. 1 would

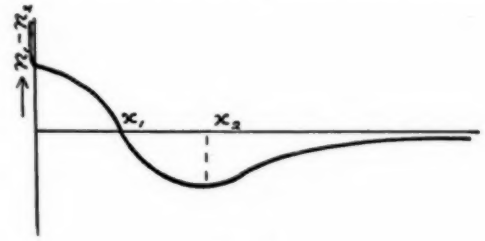


Fig. 1.

be obtained from general considerations for the case that an excess of positive ions exists in the immediate vicinity of the plate. The ordinate corresponding to $x = 0$ gives the positive charge on the plate, while the ordinate corresponding to $\delta x$ gives the excess of positive ions close to the plate. At the point $x = x_1$ the concentrations of the different ions are equal to each other, and at the point $x = x_2$ the excess of negative ions passes through a maximum. For greater values of $x$ the excess of negative ions rapidly decreases, and when $x = \infty$ the excess is zero, the curve being asymptotic to the $x$ axis at this point. It may happen in some cases that more than one maximum exists corresponding to $x = x_2$, and that maxima and minima may occur between $x = 0$ and $x = x_1$.

If an excess of negative ions occurs close to the plate, a similar state of affairs exists. We may then suppose that the curve represents the relation between $n_2 - n_1$ and $x$.

It appears from the foregoing results that if the layer of solution is infinitely thick, strictly speaking this holds also for the transition layer. But the greater part of the change in the layer evidently takes place over a small thickness, which may for convenience be taken to be equal to $x_2$ in Fig. 1.

If the concentration for each kind of electrical charge were plotted against distance from the plate two curves of the general form shown in Fig. 2, would be obtained. Each curve may, of course, have more than

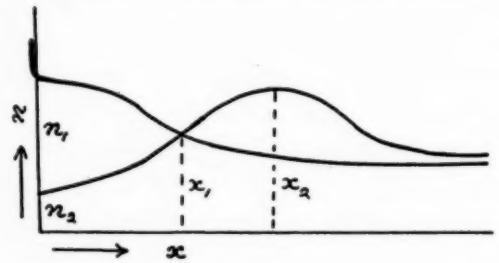


Fig. 2.

one maximum or minimum such as indicated.

The differential equations of the transition layer may immediately be formulated. The electric field $X$ acting towards the plate at any point in the layer is given by

$$X = \frac{4\pi\rho}{K},$$

where $\rho$ denotes the density of the electric tubes of force, and $K$ the inductivity of the liquid. On differentiating this equation with respect to $x$ we have

$$\frac{dX}{dx} = \frac{4\pi}{K}\frac{d\rho}{dx} - \frac{4\pi\rho}{K^2}\frac{dK}{dx}$$

or

$$\frac{dX}{dx} = \frac{4\pi}{K}(n_1 - n_2)e - \frac{X}{K}\frac{dK}{dx}, \qquad (1)$$

since

$$\frac{d\rho}{dx} = (n_1 - n_2)e,$$

where $e$ denotes the charge on an ion. The current at right angles to the layer towards the plate, which is caused by the motion of the ions due to the action of the electric field, the action of the molecular forces, and the motion due to diffusion, is zero, and hence

$$(X + F_1)n_1e + eD_1\frac{dn_1}{dx} + (X - F_2)n_2e - eD_2\frac{dn_2}{dx} = 0, \qquad (2)$$

where $D_1$ and $D_2$ denote the coefficients of diffusion of the positive and negative ions respectively, and $F_1$ and $F_2$ the forces respectively acting on the positive and negative ions toward the plate due to the asymmetrical distribution of the neutral molecules. The algebraical gain in ions of one sign per c.c. through diffusion, dissociation of neutral molecules, recombination of ions of different signs, and the velocity given to the ions by the electric field and molecular forces, is zero, and hence

$$d\frac{[(Xe + F_1)k_1n_1e]}{dx} - D_1\frac{d^2n_1}{dx^2} - \gamma + \alpha n_1n_2 = 0, \tag{3}$$

$$d\frac{[(Xe - F_2)k_2n_2e]}{dx} - D_2\frac{d^2n_2}{dx^2} - \gamma + \alpha n_1n_2 = 0, \tag{4}$$

where $\gamma$ denotes the number of neutral molecules dissociating per c.c. into ions per second, $\alpha$ the coefficient of recombination, and $k_1$ and $k_2$ the mobilities of the positive and negative ions under unit force respectively. Since the total positive charge on plate and solution is equal to the negative we also have

$$\int_0^{x_a} n_1 \cdot dx = \int_0^{x_a} n_2 \cdot dx \tag{5}$$

if a slab of solution in contact with the plate of thickness $x_a$ is considered.

The foregoing differential equations refer to the ions in the transition layer and the charge on the plate. The differential equations referring to the undissociated molecules of the solute are

$$F'N' + D'\frac{dN'}{dx} = 0, \tag{6}$$

$$d\frac{(F'k'N')}{dx} - D' \cdot \frac{d^2N'}{dx^2} + \gamma - \alpha n_1n_2 = 0, \tag{7}$$

where $D'$ denotes the coefficient of diffusion of the molecules, $N'$ their concentration, and $k'$ the mobility of a molecule under the force $F'$ due to the surrounding molecules and ions. The differential equations referring to the molecules of the solvent are

$$F''N'' + D''\frac{dN''}{dx} = 0, \tag{8}$$

$$d\frac{(F''k''N'')}{dx} - D''\frac{d^2N''}{dx^2} = 0, \tag{9}$$

where the meaning of the symbols $F''$, $N''$, $k''$, and $D''$, is obvious from the context. The quantities $D_1$, $D_2$, $k_1$, $k_2$, $F_1$, $F_2$, etc., depend on the density, etc., of the solution, and therefore on $x$. Since the forms of these functions are not known, the complete solution of the differential

equations is obviously not immediately possible. But even if they were known a complete solution does not seem realizable except in special cases. The subject will be considered more fully in a separate paper, in connection with the experimental facts.

The e.m.f. between plate and solution will also be subject to thermodynamical conditions which involve the variables internal energy, tempterature, volume and external pressure. These conditions need not concern us here since the e.m.f. would be subject to them whatever its cause. This aspect of the subject will be found fully treated in Winkelmann's Handbuch des Physik, II. ed., pp. 801–814.

A few additional remarks should be made in connection with Nernst's solution pressure hypothesis. Nernst [1] has expressed the difference of potential $E$ between a metal and solution in the form

$$E = -RT \log P_s + C,$$

where $P_s$ denotes the osmotic pressure of the metal ions in the solution, and $C$ an integration constant. The equation may also be written

$$E = RT \log \frac{P}{P_s}, \qquad (10)$$

where $P$ is of the nature of a pressure, and which has been called by Nernst the solution pressure of the metal, or the tendency of the metal to go into solution. But this tendency, we have seen, depends on the electric field of the liquid transition layer adjacent to the plate, which influences the collision of the ions of the solution with the metal. Thus in the proposed theory the nature and cause of an apparent solution pressure of a metal is the adjacent liquid transition layer.

The foregoing theory deals only, it should be noted, with the e.m.f. whose production and action is attended by chemical changes in the solution. The contact e.m.f. due to the differences in concentration of the free electrons in metals, etc., accordingly is not included. The e.m.f. of a cell as measured in practice is equal to the sum of these two electromotive forces. For the theory of the latter e.m.f. the reader may consult The Electron Theory of Matter by O. W. Richardson.

Some very important deductions can immediately be made from the foregoing theory of the e.m.f. of a voltaic cell without obtaining the solution of the differential equations of the e.m.f. of the transition layer. These will now be pointed out.

(*a*) Since according to Fig. 1 the transition layer is, strictly speaking, infinitely thick, the e.m.f. between two plates in a solution should depend to a certain extent on the distance between them.

[1] Theoretische Chemie, by Walther Nernst, VII. ed., p. 784.

(*b*) An alternating current sent through the solution and plate should change the e.m.f. of the transition layer associated with the plate. The way in which this is brought about will best appear from considering a special case. Let us consider a solution of $CuSO_4$ in contact with a Cu plate, and let us suppose that an excess of Cu ions, which are positive, occur in the immediate vicinity of the plate, in which case the e.m.f. of the layer acts in a direction away from the plate. Therefore when the direction of the current is towards the plate copper will be deposited. On the current being reversed the copper deposited will not go into solution in the reverse manner. Copper will go into solution only as $CuSO_4$ through the interaction with $-SO_4$ ions, and this solute will then gradually dissociate into + Cu and $-SO_4$ ions. Accordingly when the layer is in equilibrium the distribution of ions is different from that when no alternating current is flowing, and a corresponding change in the e.m f. of the transition layer would result. On breaking the current the layer would require a definite time to attain its original condition, which might be measurable.

A consequence of the foregoing result would be that the capillary electrometer should show a deflection under the action of an alternating current. It would also follow that the velocity of colloidal particles carried along by an electric current would experience a change in velocity on impressing an alternating current upon the direct current. An alternating current would also affect the precipitation of colloidal particles. Furthermore, electrical endosmose would be affected by a simultaneous application of an alternating current.

(*c*) A direct current sent through a transition layer would change its e.m.f. We have seen that the distribution of the ions in a transition layer is such that the velocity of migration of the positive ions, which is due to the action of the electric field, the molecular field, and diffusion, is equal to that of the negative ions at all points. Now when a direct current is sent through the layer an external field is impressed upon it, and hence a redistribution of electrical charges must result in order that the foregoing conditions may still hold. This would accordingly be attended by a change in the e.m.f. of the layer which exists apart from that due to the current.

On breaking the current it would take some time for the layer to regain its original distribution of electrical charges, and hence its original e.m.f. This might be made the basis for detecting the effect, and to a certain extent measuring it.

It follows from the foregoing result that the e.m.f. of a cell should change somewhat with the current furnished by it. The effect would

evidently be the smaller the smaller the e.m.f. of the layer due to the passage of the current is in comparison with that due to a segregation of electrical charges.

(*d*) If a metal plate is suddenly plunged into a solution, the transition layer would not be formed instantaneously, but the process should take some time. Therefore, if two plates $A_1$ and $A_2$ of the same kind of metal were connected with a galvanometer, one plate to each terminal, and the plate $A_1$ be immersed in a solution for some time, a sudden deflection should be obtained on plunging the plate $A_2$ into the solution. This would be mainly due to the e.m.f. of the transition layer associated with the plate $A$ since the layer of the plate $A$ would take some time to form. The transition layer of air next to a plate before immersion may have an e.m.f. associated with it whose magnitude is not negligible in comparison with that of the liquid transition layer on immersion, in which case it would be necessary to work in a partial vacuum. The direction of the current obtained would in any case furnish interesting information in connection with the transition layer of each plate under various conditions.

(*e*) If one of the plates at the end of the foregoing experiment be removed from the solution for a time, a transition layer having an e.m.f. associated with it would gradually be formed on the *surface* of the solution adhering to the plate. Hence when the plate is suddenly returned to the solution a deflection would be obtained corresponding to the e.m.f. of the surface transition layer of the solution. The results obtained would be independent of the nature of the metal plates used.

(*f*) If two rods of the same material but different diameters be inserted into the same solution, the transition layers would not be the same in the two cases on account of the difference in radius of curvature of the rods. Hence an e.m.f. would exist between the two rods equal to the difference between the e.m.f.'s of the transition layers. It would, however, be of appreciable magnitude only if the radius of one of the rods is extremely small.

(*g*) The e.m.f. of a transition layer would obviously be affected by the application of an external pressure upon the solution. If this is done suddenly the e.m.f. of the layer might undergo a succession of interesting changes before equilibrium is reached due to the rearrangement of the electrical charges.

(*h*) The e.m.f. of a transition layer would be affected by a change in temperature, since this would change its density, etc.

(*i*) On giving a motion to a solution parallel to the surface of an immersed plate, a part (at least) of the transition layer associated with

the plate would be carried along and be replaced by electrically unpolarized solution which in turn would tend to get more or less electrically polarized before it is itself carried away. Thus the e.m.f. of the transition layer would be different under these conditions from that existing when the liquid is at rest.

(*j*) A magnetic field applied to a plate immersed in a solution would change the e.m.f. of the transition layer, since it would affect the coefficients of diffusion of the different ions.

(*k*) The application of a stretching force to a metal plate immersed in a solution would change the e.m.f. of the transition layer. For such a treatment would change the molecular or atomic arrangement of the metal plate, and hence modify the forces exerted by the plate on the solution.

(*l*) The addition of a non electrolyte to a solution would change the e.m.f. of the transition layer, since this would change the values of $D_1$, $D_2$, $k_1$, $k_2$, $F_1$, $F_2$, etc.

The foregoing effects might be experimentally investigated in various ways. Investigations are at present in progress, the results of which will be published in subsequent papers.

THE PHYSICAL LABORATORY,
UNION COLLEGE,
SCHENECTADY, N. Y.

# THE VARIATION OF THE RESIDUAL IONIZATION IN AIR WITH PRESSURE, FOR A RANGE OF 57 ATMOSPHERES.[1]

BY K. MELVINA DOWNEY.

SYNOPSIS.

*Residual Ionization in a Closed Spherical Steel Vessel One Foot in Diameter, for Pressures up to 58 Atmospheres.*—The present work is an extension of previous experiments in which a linear relation was found between rate of ionization and pressure up to 22 atmospheres. Essentially the same method and apparatus was used as before. Results for air from 9 to 17 days old are given in curves. From 2 to 27 atmospheres, the rate of ionization increased linearly with the pressure at the rate of about 1.25 pairs of ions per c.c. per second per atmosphere change of pressure. Between 27 and 47 atmospheres the curves differ somewhat, the slope seeming to decrease with age, but above 47 atmospheres all curves are approximately horizontal, that is, the ionization was found to be practically independent of the pressure from 47 atmospheres up to the highest pressure tried. In view of the theoretical conclusions already established by Professor Swann this result clearly proves that the ionization due directly or indirectly to the action on the air of a penetrating cosmical or other radiation is extremely small, less than 0.1 pair of ions per c.c. per second at any pressure. Of the ionization produced at atmospheric pressure, about 1.25 pairs per c.c. per second must be due to radiations, either primary or secondary, coming from the walls of the vessel and having penetrations of from 28 to 47 ft. in air at atmospheric pressure; the rest must be due chiefly to much softer radiation, also from the walls. In the previous experiments performed outdoors over water instead of in the laboratory, the change of the rate of ionization with pressure was 1.56 instead of 1.25. The difference may be due to screening action by the laboratory building.

*Ionization Due to the $\gamma$ Rays of Radium in Air in a Closed Spherical Steel Vessel One Foot in Diameter, for Pressures Ranging up to 57 Atmospheres.*—A curve obtained with 2 mg. of lead-shielded RaBr placed 8 feet from the vessel, shows a slope which constantly decreases as the pressure increases, the slope at 50 atmospheres being about one eighth of the slope at one atmosphere. Evidently most of the ionization is due to secondary radiation from the walls.

## INTRODUCTION.

THE present investigation is a continuation to higher pressures of a previous experiment,[2] in which the residual ionization in air in a sphere having an internal diameter of one foot was found to be a linear function of the pressure up to twenty-two atmospheres. The experiments were undertaken for the purpose of gaining information as to the type of radiation responsible for the residual ionization. The linear relation obtained would indicate that the ionization was due either to a

[1] Presented at the annual meeting of the American Physical Society in Chicago, December 28–30, 1920.

[2] PHYS. REV., Vol. 16, pp. 420–437, 1920.

direct action of an external radiation, or to a secondary corpuscular radiation emitted from the walls of the vessel and having a penetration of at least twenty-two feet at one atmosphere. The results obtained by other observers on "Residual Ionization" were discussed in the previous paper.

## Apparatus and Method.

In the earlier work the central systems of two similar spherical ionization chambers were connected together and to a fiber electrometer, while the outer walls of the chambers were connected to opposite ends of a high potential battery. This battery was shunted with a resistance of ten megohms, and the midpoint of this resistance was connected to the case of the electrometer, in order to eliminate completely the effect of any fluctuations of the potential of the batteries. In the present experiments it was found advisable to replace the 10-megohm resistance by adjustable wire resistances immersed in oil as these remained more constant under rather trying conditions. Furthermore a sliding connection with the earth terminal was arranged so that, in case of any irregular changes in the various resistances, the earthing point [1] could easily be kept connected to the electrical midpoint of the resistances.

With a few exceptions, the details of the pressure arrangement were the same as in the earlier work. The pressure in one sphere was varied, while that in the other sphere was kept atmospheric. The pressures recorded in this paper refer to the excess over atmospheric just as in the previous paper. In the case of the high-pressure ionization sphere, it was necessary to replace the bolts holding the hemispheres together by bolts of larger cross-sectional area. During the course of the work, several imperfections appeared on the plane surfaces of the cross-sections of the hemispheres, so that considerable difficulty was experienced in finding suitable material for the gaskets. Copper was found unsatisfactory and rubber was finally resorted to.

The method of measurement differed in no essential way from that given in the previous paper. The capacity of the system was found to be 27.4 e.s. units.

## Saturation Voltage.

Thorough tests for the saturation voltage were made. The potentials given to the ionization spheres and the corresponding values for $q$, the number of pairs of ions per c.c. per second, are shown in Table I.

[1] It is convenient to speak of the common point to which all the shields, etc., were connected as the earthing point, although actual connection of this point to earth is, of course, unnecessary.

TABLE I.

| Potential in Volts. | $q$ | | |
|---|---|---|---|
| | Pressure 52 Atmospheres. | Pressure 53 Atmospheres. | Pressure 56.7 Atmospheres. |
| 120 | 42.4 | 42.4 | |
| 200 | 45.5 | 49.8 | |
| 320 | 50.4 | 50.4 | |
| 400 | 51.3 | 51.2 | |
| 520 | 51.5 | | |
| 600 | 51.5 | 51.5 | 54.9 |
| 760 | 51.5 | | |
| 800 | — | 51.7 | 54.8 |

It is evident from this table that 500 volts was ample for saturation. The potential on the spheres in the actual experimental work was from 700 to 800 volts.

RESIDUAL IONIZATION CURVES.

The graphs given in Figs. 1, 2, 3, 4 represent the change in residual ionization when the pressure excess over atmospheric was varied from zero to a value of the order of 57 atmospheres. A linear relation having a constant slope from one atmosphere to a pressure of the order of 27 atmospheres is shown by all four curves in agreement with the writer's former results. The decided drop in ionization below one atmosphere was undoubtedly due to easily absorbable radiation.

TABLE II.

| Figure. | Age of Air. | $\Delta q$ for $AB$. | Pressure at $B$. | $\Delta q$ for $CD$. | Pressure at $D$. |
|---|---|---|---|---|---|
| I..... | 17 days | 1.23 | 27.7 | 0.58 | 45.6 |
| II..... | 14 " | 1.31 | 26.3 | 0.70 | 46.5 |
| III..... | 10 " | 1.20 | 26.3 | 0.84 | 47.0 |
| IV..... | 9 " | 1.22 | 27.5 | 1.06 | 43.8 |
| Average..... | | 1.25 | 27.0 | 0.79 | 45.7 |

The values for the change in the number of pairs of ions produced per c.c. per second for a change of pressure of one atmosphere are given for each of the curves in Table II., where they are designated by $\Delta q$. The air was left in cylinders for some time before each set of observations so as to allow radioactive emanation to decay, but, as will be seen from Table II., $\Delta q$ shows no variation for the region $AB$ of the curves for an increase of the time of ageing from 9 to 17 days. This confirms the

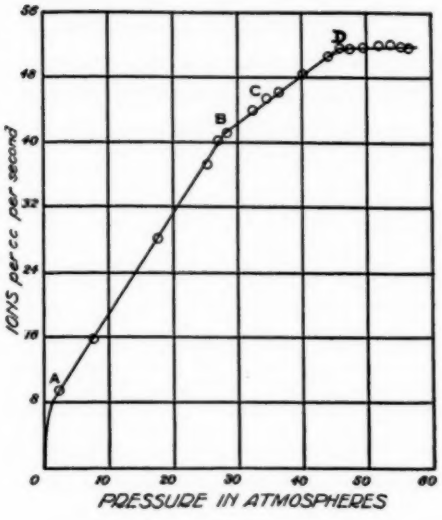


Fig. 1.

Residual ionization in air 17 days old.
1 P.M., Sept. 2, to 5:15 A.M., Sept. 3, 1920.

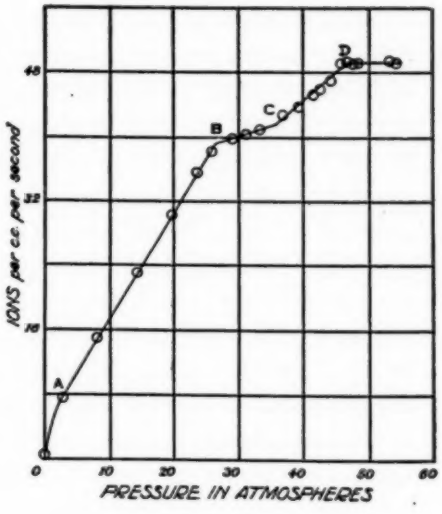


Fig. 2.

Residual ionization in air 14 days old.
4 P.M., Aug. 30, to 12 noon, Aug. 31, 1920.

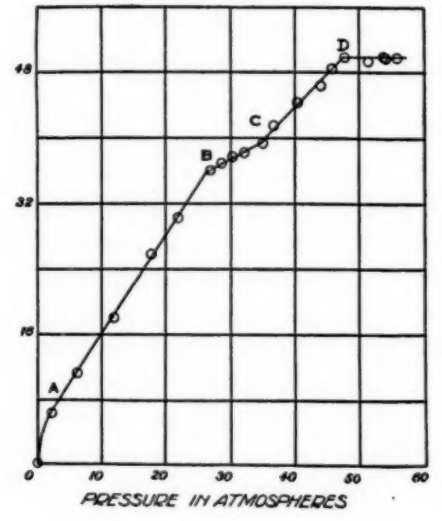


Fig. 3.

Residual ionization in air 10 days old.
5 P.M., Aug. 19, to 10 A.M., Aug. 20, 1920.

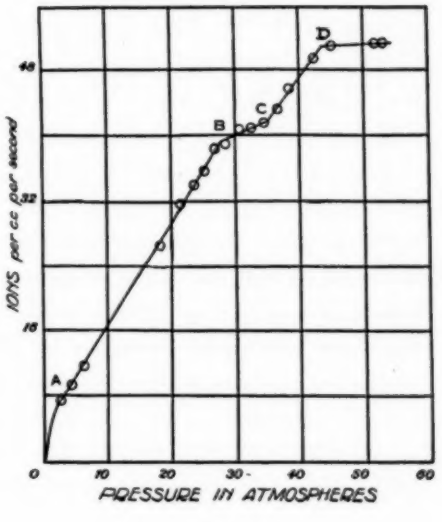


Fig. 4.

Residual ionization in air 9 days old.
10:50 A.M., Aug. 17, to 8 A.M., Aug. 18, 1920.

results of the preliminary experiments, for some of which the air was aged as long as 90 days. The effect of any small amount of emanation, which may be present, is masked then by the larger portion of soft radiation for the portion $AB$ of the curve, but an examination of $\Delta q$ for the portion $CD$ gives a suggestion of an effect due to the emanation. (It may be noted that Curve IV., for which there was the shortest period of ageing, shows a greater deviation than any other curve from the average values in the last two columns of Table II.).

Emanation may also be in part responsible for the rather irregular changes in slope shown particularly by Curves 2, 3, and 4, which correspond to the smaller periods of ageing. This would seem probable because, before taking the readings at the higher pressures, it was not always possible to wait the required time for the old decay products of any emanation present to come into equilibrium with the new amount remaining after a part of the air was expelled. The result of this would be to cause the ionization after releasing the pressure to be greater than the normal value corresponding to the lower pressure. The difference would depend upon the interval elapsing between the change of pressure and the recording of the reading, and would consequently tend to cause more or less irregular changes in slope of the curve obtained. It is of interest to observe that these changes are conspicuously absent in the case of Curve 1, which corresponds to the longest period of ageing.

The curves agree in that they indicate an upper limit for the ionization, and this is attained at a pressure of the order of 46 or 47 atmospheres. The ionization was apparently constant for the remaining range of pressures tried (approximately 47 to 57 atmospheres). The *significance of the attainment of an upper limit* beyond which the ionization does not increase with further increase of pressure was pointed out by Professor W. F. G. Swann in a paper presented before the American Geophysical Union, Washington, D. C., April 18, 1921.[1] Professor Swann has shown that the minimum increase of ionization per c.c. per atmosphere, as measured for any pressure, is greater than any portion of the ionization per c.c. per second at one atmosphere, due to the direct action of a penetrating radiation and its accompanying secondary radiation produced in the gas. (In this proof the radiation was assumed to have a penetration comparable with that ordinarily assigned to a cosmical-penetrating radiation.) In view of the preceding conclusion, the fact that an upper limit is obtained for the ionization at the higher pressures indicates that no appreciable part of the ionization at atmospheric pressure is produced by the direct or indirect action on the gas itself of a radiation of a highly

[1] Bulletin of the National Research Council, No. 17, pp. 65–73, 1922.

penetrating type. Most if not all of the ionization then appears to be due to the direct action of a radiation of a penetration low compared with that usually attributed to the cosmical radiation. It is probable that this is radiation of the corpuscular type emitted from the walls of the vessel by impurities or by the primary radiation. The ionization pressure curves indicate that the radiation is completely absorbed at pressures above 47 atmospheres.

In the previous experiments performed over the Mississippi River in 1919 with a range of pressure from zero to 22 atmospheres, the values obtained for $\Delta q$ on May 16 and May 17 were 1.55 and 1.58 ions per c.c. per second per atmosphere increase respectively. Since in these experiments the radiation from the soil was absorbed by the layer of water, it is apparent that in the present experiments (where lower values for $\Delta q$ were obtained) the walls of the laboratory building served to screen away more of the shorter range radiation in the atmosphere.

Even the average value for $\Delta q$, 1.25 pairs of ions per c.c. per second, obtained from the portion $AB$ of the curves of Figures I., II., III., and IV. (Table II.), is lower than the values at atmospheric pressure that have been given by other observers. McLennan and Murray found that 2.6 pairs of ions per c.c. per second were produced at atmospheric pressure in a vessel of ice.[1] Up to the present time this appears to be the lowest value obtained by direct measurement, but it may be noted here that Gockel estimated an approximate value as low as 1.66 for the number of pairs of ions produced per c.c. per second at atmospheric pressure.[2] McLennan and Murray seem to favor the view that this ionization is due to radioactive impurities in the material of the ionization chamber. In the light of present experiments it would be of interest to compare the penetration of the radiation given off by more common radioactive substances. Sodium and potassium are, of course, common impurities. While there have been experiments by N. R. Campbell indicating that potassium is radioactive, there seems to be no definite information as to any radiation which may be emitted.

## "Radium" Curves and General Deductions.

In the writer's work for the sake of comparison it seemed best to repeat the ionization pressure experiments with radium-bromide placed 8 feet from the inoization spheres. The values thus obtained are given in Curves V. and VI. A two-milligram sample of radium-bromide enclosed in a lead box (walls of which were 1.5 cm. in thickness) was used for these

[1] Phil. Mag., 30, p. 428, 1915.

[2] Phys. Zeit., 16, pp. 345-352, 1915.

experiments, but when the values for Fig. 6 were obtained, the radium bromide was shielded by additional plates of lead. It is evident from the graphs that the ionization values for the curve of Fig. 5 are greater than

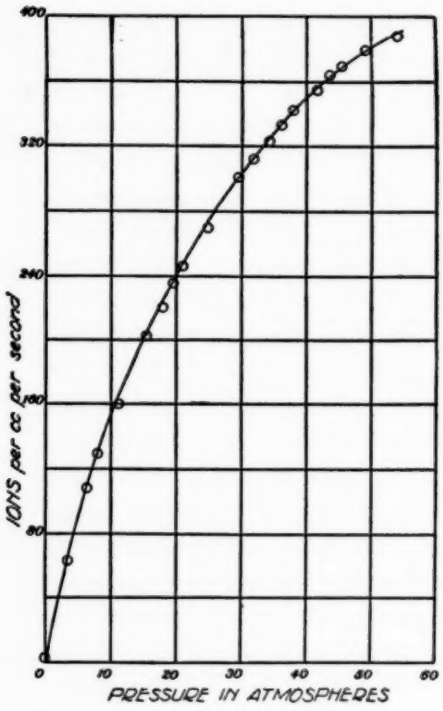


Fig. 5.

Ionization due to the gamma rays of radium.

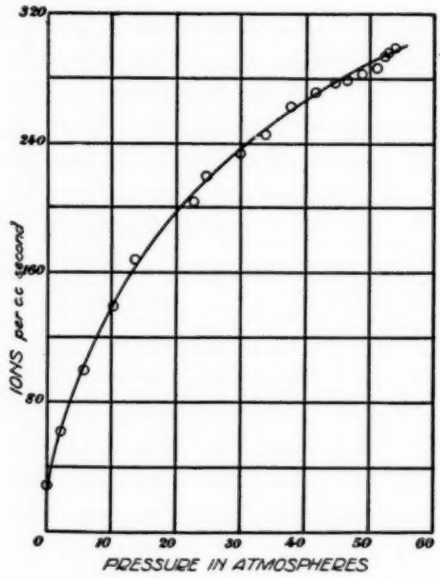


Fig. 6.

Ionization due to the gamma rays of radium. The shielding of the radium bromide used was greater for these observations than for those of Fig. 5.

those for the same pressures in the curve of Fig. 6, which of course represents ionization due to the harder type of radiation.

It is apparent that the upper limit of the ionization shown by the "residual ionization" curves is not to be found in the "radium" curves.

So far as the residual ionization at atmospheric pressure is concerned, it is obvious that the ionization due to the action of the penetrating radiation on the gas itself is practically immeasurable. It would seem than that the residual ionization must be attributed for the most part either to radiation emitted by impurities in the walls of the vessel or to secondary radiation from these walls.

This experimental work was carried on during the summer of 1920 in

the University of Minnesota. I am indebted to Professor F. B. Rowley, of the experimental engineering laboratories, for the calibration of the pressure gauge used in these experiments, and to the department of physics for the use of the laboratory facilities. I wish to express my most sincere thanks to Professor W. F. G. Swann, who has suggested this problem and given me much helpful advice throughout the course of this work.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
December, 1921.

# PROCEEDINGS

OF THE

# AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE SALT LAKE CITY MEETING, JUNE 23, 1922.

THE 115th regular meeting of the American Physical Society was held at the University of Utah at 9:30, June 23, 1922, in connection with the annual meeting of the Pacific Division of the American Association for the Advancement of Science.

Professor Orin Tugman presided.

About fifty members and friends were in attendance.

The following papers were presented, four being read by title:

1. Symmetry of Emergent and Incident Photoelectronic Velocities. ROBERT J. PIERSOL.

2. The Electrical Conductivity of Metallic Films when Exposed to Ultra-Violet Light. ORIN TUGMAN.

3. The Capillary Potential Function and its Relation to Irrigation Practice. WILLARD GARDNER, O. W. ISRAELSON, N. E. EDLEFSEN, and HARRY CLYDE.

4. A New Method of Mechanical Analysis of Soils. D. S. JENNINGS, M. D. THOMAS, and WILLARD GARDNER.

5. Test of Coagulative Power by Means of the Centrifuge. E. F. BURTON and J. E. CURRIE.

6. Energy Distribution in X-Ray Spectra. PAUL KIRKPATRICK.

7. The Limiting Frequency of the Photoelectric Effect. RICHARD HAMER.

8. The Absorption of Light by Sodium Vapor. GEORGE R. HARRISON.

9. The Relative Deposition of Radium and Barium Salts as a Function of Temperature and Acidity. W. B. PIETENPOL.

10. Breaking an Inductive Circuit. W. P. BOYNTON.

11. Radii of the Atoms of the Alkali Metal Vapors. S. H. ANDERSON.

12. The Hygroscopicity of Soils. M. D. THOMAS.

13. A General Method of Determining the Adiabatic Invariants of Mechanical Systems. V. F. LENZEN.

14. An Extension of the Principle of the Diffraction Evolute and Some of its Structural Detail. G. G. BECKNELL and JOHN COULSON.

The abstracts of the papers in the above program, with corresponding numbers, are given on the following pages.

E. P. LEWIS,
*Local Secretary for the Pacific Coast.*

## 1. Symmetry of Emergent and Incident Photoelectronic Velocities.

By Robert James Piersol.

When ultra-violet light from a Cooper-Hewitt lamp strikes a platinum film sputtered on quartz, results show that the percentage of asymmetry between the emergent and incident velocity of photo-electrons decreases directly with decrease in reflected light. These results are checked with visible mono-chromatic light, using an argon-filled Kunz photo-electric cell of which the inner lining is potassium.

A guard ring type of photo-electric cell is so constructed as to eliminate any light from being reflected to the receiving gauze. The film may be rotated through 360 degrees. Using mono-chromatic light on the platinum film the photoelectronic velocity remains constant in emergent and incident positions as well as when rotated by ten-degree intervals throughout the circle.

These results are in accordance with theoretical considerations of the quantum theory which lead to the conclusion that photo-electrons are emitted from the parent atoms, due to the storing up of definite quanta of energy, thereby imparting to the photoelectrons a velocity independent of the direction of the exciting light.

Department of Physics,
University of Pittsburgh.

## 2. The Electrical Conductivity of Metallic Films when Exposed to Ultraviolet Light.

By Orin Tugman.

Metallic films formed on mica by cathode deposition were made of such thickness that their conductivity could be determined by measuring the time of charging a quadrant electrometer through them. The films were placed in a vacuum and exposed to the light so as to reduce the conductivity due to ionization by the light. Later this source of error was found not to be a serious factor and the films were exposed to the light in the air.

When the electrometer was charged positively through the film with the light on, the time of charging was less than when the light was off, and when the electrometer was charged negatively under the same conditions the time of charging was greater depending on the potential applied. This result may be explained by the photo-electric effect.

The conductivity of the film decreased with time when the current was on. A reversal of the current showed the film to have a greater conductivity which decreased with time until the current was reversed again. Data showing this result and the time of charging the electrometer positively and negatively with light on the film were obtained.

University of Utah.

### 3. THE CAPILLARY POTENTIAL FUNCTION AND ITS RELATION TO IRRIGATION PRACTICE.

BY WILLARD GARDNER, O. W. ISRAELSEN, N. E. EDLEFSEN, AND HARRY CLYDE.

THIS paper is an attempt to apply quantitative methods to the solution of physical problems encountered in irrigation practice.

It is shown that there exists a capillary potential increasing continuously with the moisture content over a wide range. For the soil at the experimental farm the following equation is found to fit experimental data:

$$(\psi + 145)(\rho - 0.173) = -42.6.$$

$\psi$ is the capillary potential measured in gram-centimeters, the origin taken at the saturation point. $\rho$ is the moisture content in grams per c.c. From this equation, with experimental data and theoretical equations previously published, it is shown that an allowance of approximately 0.25 cm. of water per day should be made for loss into the deeper soil.

The apparatus used consists of a porous cup closed with a water-tight joint and connected through a tall tube to an exhaust pump. The cup is surrounded by a thin layer of soil in an outer vessel and atmospheric pressure maintained on the soil side. The pressure is then reduced on the water side and measured, and by means of the glass tube the amount of water in the soil is determined.

UTAH AGRICULTURAL EXPERIMENT STATION.

### 4. A NEW METHOD OF MECHANICAL ANALYSIS OF SOILS.

BY D. S. JENNINGS, M. D. THOMAS AND WILLARD GARDNER.

THIS method consists in shaking a deflocculated soil suspension in a cylindrical vessel and determining the concentration at measured distances below the surface as it changes with the time. It involves the assumption that the particles fall as individuals at a constant rate.

Since the suspension density $q$ at a point at distance $h$ beneath the surface is due to the presence of a large number of different sized particles and the decrease in this density with the time results from the disappearance, one by one, of the separate species, the concentration of any species will remain constant at this point until those particles of this species originally at the surface have fallen through the distance $h$.

The "equivalent" radius $r$ of the particles of the species vanishing at point $h$ at time $t$ is obtained from Stokes's equation and the experimental curve made to represent $q$ as a function of $r$. Then, from the relation,

$$q = k\int_0^r w\,dr$$

or

$$dq/dr = kw$$

(where $w$ is the weight of soil corresponding to $r$ and $k$ is a proportionality factor) the value of $w$ for any value of $r$ may be obtained.

Analysis of two soils by this method and a standard method gave good agreement.

UTAH AGRICULTURAL EXPERIMENT STATION.

### 5. TEST OF COAGULATIVE POWER BY MEANS OF THE CENTRIFUGE.

BY E. F. BURTON AND J. E. CURRIE.

QUANTITATIVE tests have been made on the amount of coagulum precipitated from colloidal solutions by additions of electrolytes when the samples have been centrifuged for a few minutes. The solution used was arsenious sulphide and the coagulant aluminium sulphate. Indications of complete coagulation are given in a few minutes, the results of which agree with the effects on the same samples when left standing for days under ordinary settling. This not only gives a quick method for testing coagulation, but there are indications of a definite gradation in the size of the arsenic sulphide particles due to the added electrolyte—a result which is well known from optical determinations on gold solutions.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF TORONTO, CANADA.

### 6. ENERGY DISTRIBUTION IN CONTINUOUS X-RAY SPECTRA.

BY PAUL KIRKPATRICK.

SPECTRUM curves were corrected for various distorting influences. Superposed orders at the larger crystal angles were separated by a study of the intensity-potential curves with fixed crystal setting. These results checked well with results from an absorption study of the complex reflections.

Energy was assumed proportional to ionization produced by complete absorption in methyl iodide vapor. Degree of completeness actually realized was determined for different wave lengths by direct measurements upon a volume of the gas. Correction was made for varying reflectivity of the rock-salt crystal by the reflection equation used by W. L. Bragg and co-workers and the values of $F$ as measured by them.[1] Absorptions by the wall of the Coolidge tube were determined from actual observations upon the tube itself.

The corrected curves should give the energy distribution at the emitting center save for absorption in the tungsten target. The final curve differs from the original in that the maximum is displaced toward longer wave-lengths and intensities of long wave-lengths are increased relatively many fold. The curves do not show good agreement with the theoretical energy distributions of Davis or of Behnken.

The x-ray tube was operated from a transformer but constant potential conditions to within one per cent. were simulated by the use of a synchronous shutter. Curves obtained without the shutter show, when corrected, no maximum within the observable range.

UNIVERSITY OF CALIFORNIA.

[1] Phil. Mag., Mar., July, 1921.

## 7. The Limiting Frequency of the Photo-electric Effect.

By Richard Hamer.

A MIRROR spectrograph was used as a monochromator. The prism was of fluorite and the concave mirror covered with a cathodic deposit of platinum. Light passing at the angle of minimum deviation entered the photo-electric cell through a narrow slit and fell on electrodes of the metals investigated, which were connected with a sensitive string electrometer.

The source was a carbon arc with cored carbons saturated with solutions of iron and other metals, giving a nearly continuous spectrum.

The metals were thoroughly cleaned with sandpaper and the cell was exhausted to a pressure of about 0.006 mm. The wave-length at which there was a sudden increase in the saturation current was taken as the limiting wave-length. Errors due to scattered light were eliminated as far as possible by screens.

The following values were determined:

| | | | |
|---|---|---|---|
| Silver | λ3391 ± 60 | Tungsten | 2615 ± 30 |
| Platinum | 2782 ± 35 | Copper | 2665 ± 30 |
| Aluminum | 3596 ± 100 | Zinc | 3426 ± 75 |
| Cadmium | 3130 ± 50 | Brass | 3426 ± 75 (with indications of increase at 2665) |
| Tin | 3185 ± 55 | | |
| Lead | 2980 ± 50 | | |
| Iron | 2870 ± 40 | CuO | 2665 ± 50 |
| Nickel | 3050 ± 50 | Methyl Violet | 2585 ± 30 |

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## 8. The Absorption of Light by Sodium Vapor.

By George R. Harrison.

THE absorption of light by sodium vapor in the visible and near ultra-violet has been studied, particularly in relation to temperature, vapor saturation and hydrogen pressure. Light from a Cd spark or electrically exploded wires was used as a source.

It was found that the continuous absorption at the limit of the principal series is intense over only a very limited range of wave-lengths, and does not extend undiminished to the extreme ultra-violet, as has been supposed. It apparently decreases rapidly with decreasing wave-length, in a manner similar to the analogous case with x-rays, although the exact function has not yet been determined.

The continuous absorption follows the line absorption very closely in changing in intensity with vapor density, so that they appear to originate in the same entity. It is unaffected by hydrogen pressure within the range 2 mm. to 400 mm.

Pictures were obtained with unsaturated vapor showing 25 members of the line spectrum together with the continuous absorption, while the band absorption was entirely absent except for a trace around the D-lines. This indicates that the band absorption may originate in a loose molecular aggregate

which is broken up on superheating. Evidence from Hackspill's vapor density determinations seems to show that such may exist.

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## 9. THE RELATIVE DEPOSITION OF RADIUM AND BARIUM SALTS AS A FUNCTION OF TEMPERATURE AND ACIDITY.

BY W. B. PIETENPOL.

IN the commercial refining of radium the radium salts are commonly purified by fractional crystallization of a radium-barium solution. In cooling from boiling to room temperature a percentage of radium largely in excess of that of the barium is deposited with the crystals.

Under similar conditions of cooling the relative amounts of radium and barium deposited have been determined at different temperatures throughout the cooling process and curves plotted. Determinations of the above nature have been made with radium-barium solutions of different acidity and the variation in the form of the curves shown.

The first crystals formed in the solution contain a larger percentage of radium than succeeding crystals. It is pointed out that the efficiency of the refining process may be increased by separating liquor and crystals at a point above room temperature. In this way the factor of enrichment is increased in addition to a saving in time.

The rate at which the solution cools is a factor in the relative amounts of radium and barium deposited. With rapid cooling a smaller percentage of radium is adsorbed than with slow cooling. Work on the nature of the adsorption of radium by barium is in progress.

UNIVERSITY OF COLORADO.

## 10. BREAKING AN INDUCTIVE CIRCUIT.

BY W. P. BOYNTON.

WHEN a switch is opened in an inductive circuit carrying an electrical currents the current decreases gradually to its final zero value during the persistence of the arc at the switch points. Obviously the resistance of the circuit i, increasing during that time from its initial finite value to infinity, and making this change continuously. This change of resistance can be represented as a first approximation by the form[1] previously used by the author for the resistance of a quenched spark,

$$R = \frac{R_1}{1 - at}.$$

For an approximate solution we may disregard, from the time of opening of the switch, both the e.m.f. acting in the circuit and the counter e.m.f. of ionization of the arc. The differential equation of the circuit then becomes

$$O = \frac{R_0}{1 - at} I + L \frac{dI}{dt},$$

[1] PHYS. REV. (2), 4, pp. 511–514.

in which separation of the variables gives the solution

$$O = -\frac{R_0}{a} ln(1 - at) + Lln \frac{I}{I_0}$$

or

$$I = I_0(1 - at)^{R_0/aL}.$$

In the particular case where $R_0/aL = 1$ or $1/a = L/R_0$, that is, when the time of persistence of the arc is equal to the relaxation time of the circuit with its initial resistance, the current falls off as a linear function of the time. For other values of the exponent the curve bows up or down, passing however through the same two end-points.

UNIVERSITY OF OREGON.

## 11. RADII OF THE ATOMS OF THE ALKALI METAL VAPORS.

BY S. H. ANDERSON.

THE radii of the valency electrons of the alkali metal vapors have been computed on the basis of the following assumptions: (1) that the ionizing potential is one half the potential of a point on the orbit of the valency electron; (2) that the distribution of the electrons in the kernel of the atom is that suggested by Bury[1] and Bohr.[2]

For the lithium atom the distance of the electrons in the kernel from the center of the nucleus is that computed by Langmuir[3] for the helium atom. For the other alkali metals the dimensions of the inner shells of electrons are computed from Bragg's[4] values of the elementary crystals of the alkaline halides.

The values obtained for the radii of the valency electrons are as follows:

| | |
|---|---|
| Lithium | $1.379 \times 10^{-8}$ cm. |
| Sodium | 1.80 " |
| Potassium | 2.21 " |
| Rubidium | 2.45 " |
| Caesium | 2.695 " |

If these values are plotted against the integral numbers 2, 3, 4, 5, and 6, the points are uniformly distributed about a straight line, showing that in passing from one metal to the next higher in the periodic table an extra electron shell is added to the atomic structure and that the shells are spaced evenly. This relationship is in better agreement with Bury's modification of Langmuir's theory than with the latter's original theory of atomic structure.

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[1] Bury, Journal Amer. Chem. Soc., Vol. 43, 1921, p. 1602.
[2] Bohr, Nature, Vol. 107, 1921, p. 105.
[3] Langmuir, PHYS. REV., Vol. 17, 1921, p. 339.
[4] Bragg, Phil. Mag., Vol. 40, 1920, p. 169.

## 12. The Hygroscopicity of Soil.

By M. D. Thomas.

Vapor-pressure measurements at 25 degrees C. have been made by the air-saturation method, on a group of soils of widely differing textures. The moisture content of each soil was varied so that the pressure data ranged from 10 to 97 per cent. of the vapor pressure of water.

The ratios of the moisture percentages of the soils at the same vapor pressure are nearly constant over this range of pressures. Heating the soil at 100° C. increases the vapor pressure at the same moisture content, while wetting and air-drying reverses this action. Each curve of the series is shifted proportionately by this process. The mechanical analyses also indicate that heating the soil makes the texture coarser.

Size-frequency distribution curves for these soils have been worked out, the observations being taken to 0.04 $\mu$ radius. The total surface per gram, calculated from these data, agrees only qualitatively with the ratios of the vapor-pressure curves. The total surface of the particles larger than 0.25 $\mu$, disregarding the smaller material, give ratios in good agreement with the vapor-pressure measurements. The data seem to bear out the idea of colloid-coated particles.

Utah Agricultural College.

## 13. A General Method of Determining the Adiabatic Invariants of Mechanical Systems.

By V. F. Lenzen.

P. Ehrenfest has introduced into the quantum theory the consideration of reversible adiabatic transformations of mechanical systems. Quantities which remain unchanged during such transformations are called *adiabatic invariants*. In his fundamental article Ehrenfest states that it would be desirable to develop a systematic method of finding adiabatic invariants for systems as generally as possible. This paper is a contribution toward that end. The problem is attacked with the aid of the theory of continuous groups. The method consists in determining the equations by means of which a given state of motion of the system may be transformed into an adiabatically related one. The infinitesimal transformation $Uf$ is derived and use is made of the theorem that a function is invariant under the group if $Uf = 0$. The method is illustrated by application to the problem of the simple pendulum discussed in Sommerfeld, Atombau, 3d ed. The variables used are the average kinetic energy $\overline{T}$ and the frequency $\nu$. The change in length of the pendulum is denoted by $a$. The transformation equations are

$$\overline{T}_1 = \sqrt{\frac{g}{g + 4\pi^2\nu^2 a}}\,\overline{T},$$

$$\nu_1 = \sqrt{\frac{g}{g + 4\pi^2\nu^2 a}}\,\nu;$$

$$Uf = -\frac{2\pi^2\nu^2}{g}\left[\overline{T}\frac{\partial f}{\partial \overline{T}} + \nu\frac{\partial f}{\partial \nu}\right] = 0$$

is the equation which $f(\overline{T}, \nu)$ must satisfy in order to be invariant under the transformation.

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## 14. AN EXTENSION OF THE PRINCIPLE OF THE DIFFRACTION EVOLUTE, AND SOME OF ITS STRUCTURAL DETAIL.

BY G. G. BECKNELL AND JOHN COULSON.

IT has been shown in a paper read before this Society[1] that the predominant figure in the diffraction patterns produced by comparatively large discs and elliptical plates when illuminated by a point source of light is *the evolute of the corresponding geometrical shadow.*

Accurate hyperbolic and parabolic plates are found to produce diffraction figures conforming to the principle just mentioned.

A $\frac{3}{4}$-inch auger bit of about 1-inch pitch ground to the form of a truncated cone produces a well-defined Arago spot at the center of the geometrical shadow when the point source of light is at the apex of the cone; but does not do so if the point source is not fairly close to this position. In the first case the shadow is strictly circular. The diffraction pattern and geometrical shadow are identical with those produced by a thin disc, but here the explanation in terms of the Fresnel zones is certainly not applicable.

The experiments described here and in the preceding paper point to the following general principle:

*Any particular form of geometrical shadow is always associated with the same diffraction pattern whatever be the diffracting object.*

A study of the structural detail of the diffraction patterns produced by discs and elliptical plates has been made. Photographs taken at distances of 20 to 30 meters from the diffracting objects reveal four series of alternate dark and bright bands each set of which is parallel to a quadrant of the diffraction evolute. The evolute itself is formed by the extremities of these bands, and consequently is not a continuous bright line.

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[1] Washington meeting, 1922.